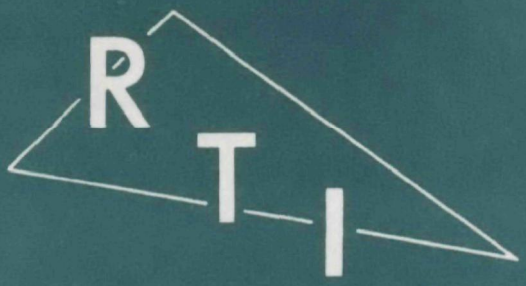

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Final Report

CONCEPTS FOR DEVELOPMENT OF FIELD USABLE TEST ATMOSPHERE GENERATING DEVICES

by

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ABSTRACT

The purpose of this project was to examine possible physical, physical plus chemical, and biological concepts applicable to the development of field usable test atmosphere generating devices. The primary activity for application of these devices is the round-robin survey to assess instrument/operator performance on a routine periodic basis. Ten concepts (i.e., desorption, effusion, thin film evaporators, novel permeation, radiolysis-photolysis, plasma discharge, thin films of dissolved reactants, electrochemical films of laminated reactants, and biological generation) were examined for each of the five required pollutants (i.e., sulfur dioxide nitrogen dioxide, carbon monoxide, ozone, and 1-butene) and a total of fifty individual discussions prepared. The program was divided into three distinct phases: (1) comprehensive literature search and preparation of technical discussions; (2) panel review of 50 discussions; and (3) comparative evaluation. Of the concepts investigated, the effusion method is recommended for generating test atmospheres for sulfur dioxide, carbon monoxide, and 1-butene, while for ozone, UV generation modified for more reliable and easier operation is recommended. Gas phase titration of nitric oxide with ozone modified for field use is recommended for generating test atmospheres of nitrogen dioxide.

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1.0 INTRODUCTION

1.1 Background/Objectives

Air pollution surveillance networks are an integral part of the total national effort to control air pollution. Regional control, source identification, episode reaction, and other elements of the control program are keyed to air quality measurements by surveillance networks. The generation and promulgation of regulatory actions are keyed to air quality data. Thus, the data from the air quality measurements have very important economic and social as well as scientific meaning. If the data are erroneous, the consequences may be costly and public confidence in the control program will be eroded.

Surveillance networks are required to monitor routinely the common pollutants which are considered as measures of air quality. These include sulfur dioxide, carbon monoxide, nitrogen dioxide, ozone, and nonmethane hydrocarbons. Because of the difficulties in measuring ambient concentrations of these pollutants, a variety of chemical and physical methods have been applied in commercially available instrumentation. These include chemiluminescent, flame photometric, infrared absorptive, gas chromatographic/flame ionization, dual-isotope-fluorescence spectrometric, coulometric, colorimetric, and other detection methods. Obviously, air quality data from these diverse instruments will be subject to many different variables with the result that the data will be of variable quality.

The validation of accuracy and hence the usefulness of data from air surveillance networks depends to a large extent upon the calibration of instruments under actual operating conditions. For continuous automated measurements, a dynamic calibration is required whereby the measuring instrument is calibrated with a known quantity of the gaseous pollutant in a test atmosphere while the system is operational in the field.

In addition to providing a basis for standardization of data, test atmospheres are required for quality control of the air quality surveillance network. The great diversity in the types of instruments, in the abilities of personnel, and in the types of organizations which are involved makes some

form of uniform quality control necessary. One way of accomplishing this is to provide, on a regular basis, samples of unknown test atmospheres to each station in the surveillance network. Each station will measure pollutant levels in the test atmosphere and report the results. Analysis of the data thus generated will provide a confidence level for air quality data from the total network, quality control on data from individual stations, and indicate points where remedial action is required.

1.2 Approach

The availability of test atmospheres thus fulfills three important functions for air quality surveillance--calibration, standardization, and network quality control. To fulfill this role, methods for test atmosphere generation must be identified and developed. These methods must (1) have a high degree of reliability, (2) be relatively immune to operator errors, and (3) be sufficiently economical to allow broad application. Several test atmosphere generation methods have received much use in instrument calibration. These include permeation tubes, quantitative gas mixtures, and UV ozone generators. While these may be prime candidates for providing broad test atmosphere generation capabilities, each has limitations that make the examination of other methods desirable.

In Section 2.0, an overall system concept for assessing the performance of an air quality surveillance network through use of test atmospheres is discussed. This includes a framework for classification of the various methods for generation of test atmospheres so that comparative evaluation can be accomplished. The operational requirements and constraints for viable test atmosphere generating methods and for an operational system employing these methods are also discussed. The modular approach in which commonalty is attained in the components of methods employed for the various pollutants is also described.

In Section 3.0, the various specific methods proposed for test atmosphere generation are described. To insure comprehensiveness, it was required that a method be considered for each of the five pollutants in each of the classifications indicated by an asterisk in Table 1-1. Even when the

Table 1-1: Classification of New Field Usable Test Atmosphere Generating Devices

Physical methods	
Desorption	*
Effusion	*
Thin film evaporates	*
Permeation (novel methods)	*
Chemical methods	
Radiolysis/photolysis/thermolysis	*
Plasma discharge	*
Thin film evaporator	*
Electrochemical	*
Laminated reactants	*
Biological	*
Other methods	+

*Required

+Optional

method appears trivial for a specific pollutant, that fact must be stated and substantiated. This requires a basic set of 50 methods. In addition, to assure comprehensiveness in the subsequent analysis, conventional methods of test atmosphere generation are also discussed and additional methods that do not conform to the classifications are included.

In order to provide common bases for evaluation, the various methods are compared in Section 4.0. The parametric measures--costs, weight, operator training requirements, logistical demands, developmental status, predicted accuracy and reliability--are employed to rank the various methods.

To identify the most promising methods and to specify the one that is recommended for development, a panel of experienced scientists and

engineers was given the data and information contained in Sections 2, 3, and 4. The results of the panel's deliberations are given in Section 4.4.

In Section 5, recommendations compounded from the panel and the project studies are presented. These consist of a recommendation of a method for each of the pollutants as well as the one method that is recommended for immediate development because of its potential present value to the air quality surveillance program.

2.0 OVERALL SYSTEM CONCEPTS

The impetus for development of field usable test atmosphere generation methods is for standardization and quality control for air surveillance networks. Emphasis is on quality control because it represents the more challenging problem and, if solved, will provide standardization capabilities for air quality data. In order to provide a basis for evaluation of test atmosphere generation methods, the operation of an optimal quality control system is described in this section. Then a basis is given for classification of the various test atmosphere generation methods and the desirable attributes of such methods are given.

2.1 Optimal Surveillance System Application of Test Atmosphere Generation Methods

The air quality surveillance system is assumed to consist of from 1,000 to 5,000 measurement stations grouped in a nonuniform pattern by area, State, and region and providing air quality data to various control agencies and data banks. In the foreseeable future, it is expected that the number of stations providing continuous reliable records will be small but growing, and that there will be a large number of stations coming on line, many of which will have sporadic records and low quality data. The problem is to provide test atmosphere generating devices, whereby the quality of the data from any monitoring station can be accessed.

Because the operation of air quality surveillance stations has been decentralized, the degree of uniformity in personnel, resources, and procedures will be minimal. This leads to considerable variation in the nature of the data that are produced, and this disparity is increased by the variety of instrumentation that is employed in data collection. Any attempt to attain uniformity in station capabilities in the near future will be difficult. Thus, the only method that can attain meaningful surveillance network operation is to determine the quality of the data produced by an independent testing procedure. The development of field usable test atmosphere generation methods that can be used to ascertain the data quality from each

of the stations is a step toward attaining a viable independent testing procedure.

In order that test atmosphere generation be accomplished by a uniform, reproducible method at each of the measuring stations, it is desirable that both a basic test atmosphere generation accessory kit and the individual test samples be provided by a central agency. The kit might consist of an air purification system, a manifold, a blower, and certain flow measuring and control devices. The samples, dependent on the method, might consist of small containers to be attached to the manifold by prescribed procedures. It would be intended that the kit would be assembled such that samples and instruments could readily be attached to it to accomplish a given test. A supply of materials such as might be used in the air purifier would also be supplied with well-defined procedures and controls for their use.

Operation, at the measuring site, would begin with receipt in the mail of a sample container and directions for its use. The operator would schedule the test at which time he would activate the air purification system and blower, attach the sample container and instrument to the manifold, and, following the procedures given, would perform the measurement. The results would be recorded on forms provided and returned to the central agency for evaluation.

The central agency, on a scheduled basis, would procure or prepare the necessary number of test samples and distribute them to the operating stations. At the end of each test the results would be recorded and provided to the air quality control data collection center to use for quality control. Each station would be provided with a record of its performance so that, if remedial action were required, it could be taken. In addition, summary data could be provided to the administrative control points of the air surveillance network for their use.

In order that such a quality control system be operable, certain restrictions on the methods for test atmosphere generation become obvious. Before examining these restrictions, however, a framework for the classification of test atmosphere generation methods will be described.

2.2 Classification of Generation Concepts

A practical test atmosphere generation system involves at least three basic functions.

1) Storage - The pollutant, either in pure or dilute form, must be stored in some enclosure for distribution and retention until the test is made. Storage may be as a gas, liquid, or adsorbed phase or may be in a chemically different form.
2) Dispensing - The stored form of the sample must be dispensed from storage at a known rate. This may be by a metering valve; by a controlled reaction; by evaporation, effusion, or permeation; or by batch techniques such as with a gas syringe.
3) Dilution - It is necessary to mix the dispensed pollutant gas with a known quantity of air to obtain the desired test atmosphere. This is accomplished in a mixing manifold in which the pollutant is mixed with air. The air must be free of interferences. This usually involves elimination of particulates and moisture, and reducing pollutant levels in the air below detection limits.

Each of the above functions is required in test atmosphere generation but, in a given method, the functions can often be combined. Thus it is desirable to examine other bases for test method classification. Since each method embodies a basic scientific principle, it is possible to use these principles for classification. Physical, physical plus chemical, and biological methods form the basis for this type of classification.

Most test atmosphere generation methods are based on physical principles. Physical storage may involve pressurized gas, entrapment of gas in a solid material, or adsorption of the gas on a surface. Physical methods for dispensing gas involve effusion, diffusion, evaporation, or permeation.

Chemical methods are based on dissociation of a compound containing the desired entity, combination of materials to form a desired compound, or an activation process. Gases such as carbon monoxide can be formed by

dissociation but characteristically in such reactions conditions must be carefully controlled to obtain the desired product. More often dissociation is applicable as one step in a two-step process wherein an elemental form is first produced and then reacted so as to combine with a second material to produce the desired product. Combining reactions are typified by oxidation of carbon, sulfur, or nitrogen to produce CO, SO_2, or NO_2. Activation is most strongly associated with the production of ozone from oxygen but also may be used as a driving force for other reactions.

There is less variety in the availability of biological methods for test atmosphere generation largely because of the complexity of these processes and the resulting difficulty in releasing the desired gaseous component from the biological system.

Because of the nature of this survey of possible test atmosphere generation methods, the latter classification scheme based on scientific principles has been adopted. It is given in Table 1-1 and is the basis for the subsequent discussion of specific methods. It must be recognized that seldom does a generation method described in this classification stand alone. More often, a combination of methods is required wherein several physical processes are combined with a chemical process to obtain a viable generation method. Then too, one process may fulfill several functions. It is not uncommon to find the dispensing and dilution functions, for example, combined in one piece of apparatus. Thus, as with any classification method, the boundaries are indistinct, and one must be alert to these shortcomings in order to realize the objective--to provide a comprehensive framework for surveying and comparing all possible generation methods.

2.3 Constraints and Objectives

The evaluation criteria for field usable test atmosphere generation methods are listed in Table 2-1. Emphasis must be on an economically viable system wherein test samples originate at a central point, the tests are run with minimum effort and minimum opportunity for error at a large number of test sites, and the results are analyzed at the central point to assess the quality of the data being generated at each station.

Table 2-1: Field Usable Test Atmosphere Generating Methods Evaluation Criteria

1)	Simplicity	The method should be usable by an untrained operator with little opportunity for error.
2)	Portability	The method should be applicable in a mode that requires no complex logistics in providing test atmospheres at many sites at frequent intervals.
3)	Cost	The material and labor costs must be minimal to allow wide use. These include costs at the central distribution point, the cost of the distributed item and costs at test sites. Where possible, costs should be incurred in the central distribution point in preference to the test site in order to amortize the costs over a much larger population of tests.
4)	Capacity	The generation method must be capable of providing 1-3 ℓ/min of test atmosphere for periods up to 2 hr.
5)	Range	The pollutant levels in the test atmosphere must range from the minimum detectable levels with the reference test methods to alert levels.
6)	Operating mode	The test atmosphere must be usable in a "blind" mode; i.e., one in which the instrument operator does not know the pollutant concentration.
7)	Accuracy	A deviation of the actual concentration from the specified concentration of $\pm$20 percent at the time of use is acceptable.
8)	Safety	The apparatus and components used to generate test atmosphere must include provisions for operator safety and transportation requirements.

2.4 Modular Approaches

In a modular approach, one attempts to integrate methods for generation of the various types of test atmospheres so that the number of components associated with each individual type is minimized. This allows a large investment in the components that are common to all of the methods with potentially beneficial effects on the overall system.

An obvious component that is common to many generation methods is the supply of clean air for dilution. Whether this is a compressed air source or an air scrubbing apparatus (the trade-offs between these should be analyzed), an air supply suitable for all types of atmospheres can be obtained with no or relatively little additional effort over that required to supply a method for one type of atmosphere.

Additional opportunities for common modules include the following:

1) Mixing chambers
2) Compressed gas storage containers
3) Effusion modules
4) Thermostatically controlled chambers
5) Power supplies for electrochemical or plasma generation methods
6) Flowmeters and valves
7) Blowers and pumps
8) Instrument manifold
9) Dispensing valves
10) Dilution systems

Component and module commonality may be sufficiently important so as to favor selection of one method over an otherwise superior method in order to enhance the capability and availability of the overall system.

3.0 SPECIFIC METHODS

Specific methods or devices for test atmosphere generation that are described in this chapter are not necessarily optimized with respect to the constraints given in Section 2.0. Rather the approach was to describe methods based on specified physical and chemical principles. The subsequent comparative evaluation and panel analysis is directed toward examining each method with respect to the defined constraints. In particular, the methods described in Section 3.1 are those currently employed for calibration of air quality instrumentation and are based primarily on technical requirements. The operational constraints of test atmosphere applications in quality control of a surveillance network have not been considered in the evolution of these.

3.1 Contemporary Test Atmosphere Generation Methods

Contemporary test atmosphere generation methods are referred to as dynamic calibration systems. These are available commercially for each of the specific pollutants being considered and are employed for the field calibration of air quality analyzers.

3.1.1 Sulfur Dioxide

A. Principle

Permeation tubes offer a simple method of preparing low level concentrations of SO_2 and are currently recommended and used to calibrate SO_2 analyzers both in the laboratory and for field applications. Permeation tubes are prepared by sealing liquefied sulfur dioxide in fluorinated ethylene-propylene copolymer (FEP Teflon). The permeation process depends primarily on dissolution of gas in Teflon, permeation through the Teflon wall, and evaporation from the outer surface. The main driving force is the difference in partial pressure between the inner and outer walls of the tube. Permeation tubes are highly temperature sensitive and require that the temperature be controlled to $\pm 0.1°C$. A permeation tube can be accurately calibrated by gravimetric or volumetric methods. After initial equilibration the permeation rate for SO_2 tubes is essentially constant

until all the liquid has been consumed. By proper selection of temperature, tube length, wall thickness, and diluent flow rate, accurately known concentrations of SO_2 can be generated in the parts-per-billion to parts-per-million range. Sulfur dioxide permeation tubes are available from several vendors, including the National Bureau of Standards, which offers a certified SO_2 permeation tube as a primary standard.

B. Physical Characteristics

A typical system is 30.5 x 45.7 x 40.6 cm and weighs 22.7 kg.

C. Operational Requirements

Permeation tube test atmosphere generators require skilled operators, a supply of clean air, and require several hours of warmup time.

D. Maintenance Requirements

Little maintenance is required.

E. Shipping Requirements

The permeation tube is small and weighs less than 10 g but a dynamic calibration system is difficult to ship because it is a precision electromechanical assembly and is easily breakable.

F. Estimated Accuracy

On the order of ± 2 percent under optimum conditions.

G. Estimated Cost

Permeation tube calibration systems are commercially available from a number of vendors (i.e., Bendix, Tracor, Analytical Instruments Development, Inc., etc.) and cost from $1,000-$2,500, depending on the options.

H. Advantages/Disadvantages

Permeation tube calibration systems are inherently expensive, require skilled operators, require precise temperature controls, lack ruggedness and portability and require several hours temperature equilibration of the bath (i.e., air or water) and the permeation tube. Advantages of SO_2 permeation tubes are accuracy (once calibrated), reliability, long life (6 to 12 months), availability, and ease of transport of the permeation tube itself.

3.1.2 Nitrogen Dioxide

A. Principle

Due to problems associated with field use of NO_2 permeation tubes, an alternate procedure (gas phase titration was developed for dynamic calibration of chemiluminescent NO-NO_x-NO_2 analyzers. The technique is based upon application of the rapid gas phase reaction between NO and ozone to produce a stoichiometric quantity of NO_2.

$$NO + O_3 \rightarrow NO_2 + O_2$$

Nitric oxide (50-100 ppm in N_2) from a pressurized cylinder is diluted with a constant flow of clean air to provide NO concentrations in the range 0.05 to 1 ppm (94 to 1880 $\mu g/m^3$) and is then used to calibrate the NO and NO_x cycles of chemiluminescent NO-NO_x-NO_2 analyzers. By incorporation of a calibrated ozone generator in the calibration apparatus upstream from the point of NO addition, precise NO_2 concentrations can be generated by oxidation of NO to NO_2 with O_3. As long as a slight excess of NO is present, the amount of O_3 added is equivalent to the amount of NO consumed and is equivalent to the concentration of NO_2 generated. Field usable calibration systems based on the gas phase titration method are commercially available and have the capability for calibration of both O_3 and NO_2 analyzers.

B. Physical Characteristics

In its commercial form, this is a 30.4 x 40.6 x 45.7 cm instrument weighing about 22.7 kg.

C. Operational Requirements

A calibrated supply of nitric oxide in an inert gas is required in addition to the normal manifold and diluent airstream.

D. Maintenance Requirements

Once operational little maintenance is required.

E. Shipping Requirements

This is a bulky electromechanical assembly which must be carefully packed for shipping.

F. Estimated Accuracy

Accuracy can be $\pm$3 percent.

G. Estimated Cost

This unit costs approximately $2,000.

H. Advantages/Disadvantages

The major advantage of the gas phase titration system is that the system can be used to generate known concentrations of O_3, NO, and NO_2. Major disadvantages are that the system is designed for calibration of chemiluminescent NO-NO_x-NO_2 analyzers (i.e., excess NO is present), is expensive, requires the services of a skilled operator, and requires the use of a cylinder of NO in N_2 and an expensive stainless steel regulator. At the present time the gas phase titration system is considered to be more reliable for field use than NO_2 permeation tubes.

3.1.3 Carbon Monoxide

A. Principle

Calibration of CO analyzers is limited to the use of calibration gases (CO in air or nitrogen), purchased in pressurized cylinders from various manufacturers (i.e., Scott, Matheson, Linde, etc.) and furnished with a certificate of analysis as to the CO concentration.

B. Physical Characteristics

The physical characteristics are related to the size and weight of the compressed gas cylinder, 1.8 kg, 5.1 cm in diameter and 38.1 cm long for a lecture bottle; 61.4 kg, 22.9 cm-diameter and 132.1 cm-length for a size 1A cylinder.

C. Operational Requirements

The cylinder can be turned on and used at any time. Most operators have familiarity with gas cylinders and regulators. A calibration and diluent airflow may be required, depending on the cylinder gas concentration and the instrument calibration inlet system.

D. Maintenance Requirements

These are nominal.

E. Shipping Requirements

Shipping of cylinders of compressed gas is required. These may vary from the small lecture bottles to large cylinders depending on usage and operational decisions.

F. Estimated Accuracy

Analysis of component concentration certified to an accuracy of ± 2 percent can be obtained from the manufacturer.

G. Estimated Cost

This is dependent on cylinder size but is approximately $100. For each location about $150 is required for regulators and flowmeters.

H. Advantages/Disadvantages

Advantages of using compressed gases are simplicity of operation, minimum setup time and immediate usage on demand. Disadvantages include acceptance of manufacturer's certification as to CO content or recalibration against the NBS standard, lack of portability, instability of CO at low concentrations (<25 ppm) in pressurized tanks (i.e., stable for approximately 6 months), safety aspects, and the need for several cylinders of different concentrations for multipoint calibrations.

3.1.4 Ozone

A. Principle

The production of a stable and reproducible concentration of ozone in air has always been a major problem in the operation and calibration of ozone analyzers. In the absence of a primary ozone standard, the calibration of ozone instrumentation has been accomplished by reference to the neutral-buffered potassium iodide method. A dynamic calibration system using an ultraviolet ozone generator is recommended for generation of test atmospheres for calibration of ozone-oxidant instrumentation. This system is currently being evaluated by the National Bureau of Standards as a secondary ozone calibration source. Briefly, the ozone source consists of an 8-inch current-controlled ultraviolet mercury arc lamp which irradiates a 5/8-inch quartz tube through which clean (compressed) airflows at 5 ℓ/min. Ozone levels from low parts-per-billion to 1.0 parts-per-million (1960 $\mu g/m^3$) can be generated by variable shielding of the lamp envelope. Recent field evaluation studies have shown that once initially calibrated (i.e., referenced to neutral-buffered potassium iodide method) the precision of generating ozone concentrations via the ozone generator is equal to or better than the precision of the measurement by the manual iodometric method.

Ozone calibration systems utilizing the low pressure mercury arc lamp are commercially available in various configurations from several vendors (i.e., Bendix, MacMillan, etc.).

B. Physical Characteristics

These are dependent on the particular design employed but can range in weight from 9.1 to 22.7 kg and in dimensions up to 30.5 x 40.6 x 45.7 cm.

C. Operational Requirements

Electrical power (115 VAC) and clean air are required.

D. Maintenance Requirements

These are nominal once the flow rates are calibrated.

E. Shipping Requirements

This is a 22.7 kg assembly.

F. Estimated Accuracy

Under ideal conditions, accuracies can be about $\pm$ 3 to 5 percent.

G. Estimated Cost

A commercial unit will cost between $1,000 and $2,000.

H. Advantages/Disadvantages

Advantages of this ozone generation system are the inherent short-term and long-term stability, portability, reliability, and ease of operation, once calibrated. Disadvantages include the requirement for reference to the manual iodometric method and the effect of flow rate and line voltage fluctuations.

3.1.5 Butene-1

Generation of test atmospheres of butene-1 for field applications can be accomplished by several methods--permeation tubes, dynamic dilution, or static dilution of a fixed volume or weight of contaminant into a fixed volume of diluent air. Static dilution systems are usually employed when comparatively small volumes are required, as would be the case for production of gas-phase standards for calibration of gas chromatographs, mass spectrometers, and infrared spectrometers. Here, microliter quantities of butene-1 would be injected into a Tedlar bag and diluted with clean air to sufficient volume to produce the desired parts-per-million concentration. Dynamic dilution would involve single or double stage dilution of butene-1 and clean air to produce the desired parts-per-million concentration. Permeation tubes which have previously been described are also available for generation of parts-per-million calibration concentrations of butene-1.

3.2 Physical Methods

The test atmosphere generation methods described in this section are based on physical processes; i.e., desorption, effusion, evaporation, and permeation. The release of the pollutant species into an air stream is determined by actual control of a flow rate occurring due to a pressure gradient or by control of the vaporization rate from a condensed form of the pollutant. It is obvious that the physical properties of the five pollutant gases are sufficiently different so as to produce a large variety in the best apparent methods.

3.2.1 Desorption

Probably no other technique has as much theoretical and practical information in the literature as the adsorption/desorption technique. In the field of chromatography in which the two phenomena are intimately involved, the following serials are published: Advances in Chromatography, Separation Science, Chromatographic Reviews, Chromatographia, Journal of Chromatography, Journal of Chromatographic Science, and Journal of Gas

Chromatography. While both physical and chemisorption processes are possible for the adsorbent-adsorbate pairs considered here, physical adsorption is thought to predominate. We base this conclusion on the chromatographic work on the considered gases and the fact that relatively low temperatures (below 100°C) are required for their total desorption.

3.2.1.1 Sulfur Dioxide

A. Principles Involved

Experimental measurements of the amount of a gas adsorbed as a function of pressure and temperature may conveniently be plotted in the form of adsorption isotherms. One such isotherm is the so-called BET isotherm which is written as follows:

$$\frac{N}{N_m} = \frac{k\ p/p_o}{(1 - p/p_o)\ (1 - (1-k)p/p_o)}$$

where

N = loading, mmol/g

N_m = monolayer loading

k = a constant

p = equilibrium pressure

p_o = vapor pressure of the bulk liquid.

If only physical adsorption on nonporous surfaces is involved, then desorption will follow the same isotherm curve upon decreasing of the pressure.

Physical adsorption and desorption per se is instantaneous; however, with adsorbents containing many fine pores or capillaries, the effective rate is governed by one or more of several diffusional steps. Broadly speaking, these may be categorized into the fluid phase and the solid phase mass transport. The fluid phase mass transport is governed by the molecular (and/or ionic) diffusivity and also eddy diffusivity in turbulent flow. The solid phase mass transport is governed by molecular diffusion,

Knudsen diffusion, and surface diffusion. Thus, when capillary condensation occurs, the adsorption isotherm exhibits hysteresis on desorption.

For desorption five basic techniques exist (Ref. 1):

1) thermal swing desorption;
2) pressure swing desorption;
3) purge gas stripping;
4) displacement desorption with a fluid less strongly adsorbed than the material being adsorbed;
5) displacement desorption with a fluid that is more strongly adsorbed than the material being desorbed.

Often a combination of some of the above basic desorption techniques is also used. In the thermal swing desorption technique, one raises the temperature of the adsorbent, and the desorption rate is governed by the rate of heat transfer to the adsorbent. Knowing the final desorption temperature and adsorbate vapor pressure permits one to predict the final adsorbate loading from equilibrium data. Pressure swing desorption is accomplished by conducting desorption under reduced total system pressure. It has the advantages of simplicity and adaptability to rapid cycling. Purge gas stripping technique operates by sweeping the desorbate away from the adsorbent, thus maintaining the partial pressure of the desorbate vapor below its equilibrium value. The amount of desorption for a given amount of purge gas depends primarily upon the equilibrium vapor pressure at the temperature and total pressure of operation. Higher operating temperature and lower total operating pressure will increase the overall desorption rate. Desorption with a purge that is less strongly adsorbed than the adsorbate is accomplished by both displacement and purge. Desorption with a purge that is more strongly adsorbed than the material being removed results in the formation of a steady-state desorption front. Behind the front the adsorbent is loaded with the adsorbable purge, and ahead of the front the desorbate, uncontaminated with the displacement purge, is available.

Of the different adsorbents that have been used in the chromatographic analysis of sulfur dioxide, we suggest the use of 40-60 mesh Teflon coated with a polyphenyl ether containing phosphoric acid (Ref. 2) for the adsorption-desorption function intended here. This adsorbent is suggested because it has been used in the chromatography of sulfur dioxide at 50°C; it apparently involves no chemisorption since it has been used in the analysis of as low as a few ppb amounts; and the materials are commercially available.

B. Physical Characteristics

Tha calibration output requirements for SO_2 have specified as 1 ppm as the upper limit with the field usable test atmosphere generating device delivering the doped air at 3 ℓ/min (upper rate) for periods up to 2 hr. Thus, the maximum volume (360 ℓ) of doped air would require 0.36 cm^3 (0.016 mmol) of adsorbed SO_2. The adsorption capacity data and sorption kinetic data for the proposed system are not available. Batchwise delivery of a known amount of SO_2 would be possible as all of the dopant can be desorbed at 50°C without apparent loss. Feasibility of a continuous delivery at the required rates would have to be established first. The chromatographic work indicates that the effects of temperature cycling upon the adsorbent efficiency are minimal.

At the instrument site, a supply or source for zero (clean) air is required. This may be either a compressed tank of clean air or an air scrubbing system. Alternatively, zero air source can be a part of the portable test atmosphere generating unit proposed.

It is proposed that stainless steel be used to fabricate the tube as this material has been shown not to adsorb sulfur dioxide (Ref. 3). For the purposes of setting upper portable unit dimensions, we assume that 5 g of the adsorbent is sufficient for storing the dopant. This amount could be packed in a tube 1 cm in diameter x 7 cm long. The entire unit including compressed zero air lecture bottle, dopant source tube, and storage bag if any (up to 360 ℓ capacity) would have the following physical characteristics:

Total weight: 3.6 kg

air lecture bottle - 2.3 kg
dopant tube - - - - 0.2 kg
valve + tubing - - - 0.2 kg
storage bag - - - - 0.9 kg

Total unit dimensions: 45.7 x 30.5 x 7.6 cm

air lecture bottle - 38.1 x 5.1 cm diameter
dopant tube - - - - 7.6 x 0.6 cm diameter
storage bag - - - - 12.9 x 12.7 x 2.5 cm when collapsed; inflated ~88 cm diameter sphere for 360 ℓ volume.

C. Operational Requirements

Any one of the five basic desorption techniques or a combination of them can be used to deliver sulfur dioxide for dilution. Thus, depending upon the choice of the desorption technique, a source of desorbing material, heat or vacuum would be needed. In case a conducting adsorbent were used, then only a source of electric power would be needed for direct coupling with the adsorbent.

If the continuous delivery of SO_2 were found to be feasible, then the operation of the unit would consist of plugging in the heater of the adsorption tube set to produce a predetermined temperature (50°C for example) inside the tube (probably less than 10 min to reach it) and adjusting of the precision valve on the compressed air bottle and/or the SO_2 adsorption tube for the desired rate of doped air delivery. This could be directed directly into the instrument manifold or in a storage bag.

D. Maintenance Requirements

No special maintenance is required.

E. Shipping Requirements

The tubes would be expected to be shock resistant and no special shipping containers would be needed for the monolayer adsorbed tubes. For the highly loaded tubes a gastight, low-pressure resistant shipping container would be needed.

F. Estimated Accuracy

The accuracy depends on the ability to measure a quantity of sulfur dioxide or on the precision of a metering valve. Differential screw-driven diaphram valves with conductances that can be adjusted to less than 10^{-14} ℓ/s are available. This rate adjustment capability is some six orders of magnitude below that required for the minimum SO_2 doping rate (1.7×10^{-8} ℓ/s). Thus, we believe an accuracy of $\pm$ 10 percent should be achievable.

G. Estimated Cost

1) Development - $50,000
2) Production - The material costs would be minor and commercial sources of SO_2 are available. However, the initial costs at each installation could be several thousand dollars.

H. Advantages/Disadvantages

This type of test atmosphere benerator could be simple to operate and have a minimum of support requirements. There are, however, a number of parameters that require investigation before the merits of this method can be evaluated.

I. Design Sketch

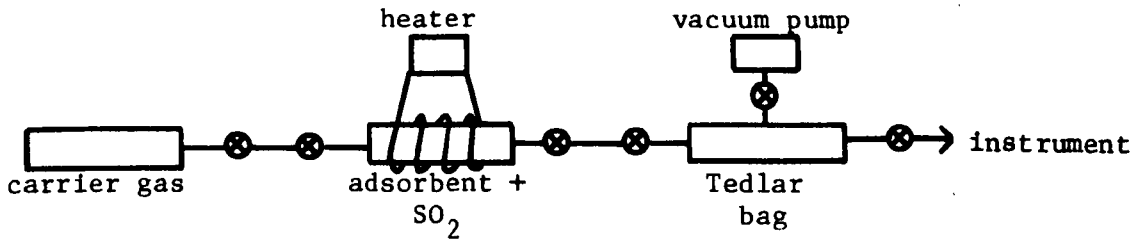


Figure 3-1. SO_2 test atmosphere generator.

J. Recommendations

Determine experimentally the feasibility of continuous doping prior to development efforts.

K. References

1. Lee, M. N. Y. In Recent Developments in Separation Science. Vol 1, Cleveland, Ohio, Chemical Rubber Co. Press, 1972, p. 75.

2. Stevens, R. K., and A. E. O'Keeffe. Anal. Chem. 42:143A (1970).

3. Wohler, H. C., H. Newstein, and D. Dannis. J. Air Pollution Control Assn. 17:753 (1967).

3.2.1.2 Nitrogen Dioxide

A. Principles Involved

All of the general and specific considerations advanced for SO_2 are equally applicable to NO_2. In addition, because of its great reactivity and tendency to undergo compositional changes, a most challenging problem in its handling is presented. The following equilibria, among others, are pertinent:

$$2NO_2 \rightleftharpoons N_2O_4$$

$$3N_2O_4 + 2H_2O \text{ (moisture)} \rightleftharpoons 2NO + 4HNO_3$$

$$NO_2 + NO \rightleftharpoons N_2O_3$$

Irreversible adsorption of NO_2 and interaction with water are two problems that have been solved in certain systems (Ref. 1). As a general rule, systems handling NO_2 require prior conditioning with the gas.

Of the different adsorbents that have been evaluated in the chromatographic analysis of NO_2 we suggest the use of Fluoropak-80 coated with 10% SF96. This adsorbent is suggested because it has been used in the chromatographic analysis (Refs. 1, 2) of a few ppm of NO_2 at room temperature and the materials are available commercially.

B. Physical Characteristics

The calibration output requirements for NO_2 are approximately those of SO_2, thus requiring 0.36 cm^3 (0.016 mmol) of adsorbed NO_2. Prior conditioning of the adsorbent with NO_2 is a requirement and neither the adsorption capacity nor sorption kinetic data are available for the system. The same delivery considerations as for SO_2 apply also for NO_2.

Stainless steel is proposed as the material to be used in the fabrication of the tube as it has been found to have adequate resistance to NO_2 (Ref. 3). Because of practically the same volumes of adsorbed gases required, the same weight and dimensional considerations as for SO_2 also apply to the NO_2 unit.

C. Operational Requirements

Same as those for sulfur dioxide except that most of the nitrogen dioxide chromatographic work has been done at room temperature.

D. Maintenance Requirements

Same as those for sulfur dioxide.

E. Shipping Requirements

Same as those for sulfur dioxide.

F. Estimated Accuracy

Same as that for sulfur dioxide.

G. Estimated Cost

1) Development - $30,000.
2) Production - Since the material costs would be minor and nitrogen dioxide is available, the unit cost should be small for adsorption sources. The initial costs for each using installation would be several thousand dollars.

H. Advantages/Disadvantages

Same as those for sulfur dioxide.

I. Design Sketch

Same as that for SO_2.

J. Recommendations

Determine experimentally the feasibility of continuous doping prior to development effort.

K. References

1. Lawson, A., and H. G. McAdie. J. of Chromat. Sci. 8:731 (1970).

2. Morrison, M. E., R. G. Rinker, and W. H. Corcoran. Anal. Chem. 36:2256 (1964).

3. Wright, C.M., and A. A. Orr. Anal. Chem. 40:29 (1968).

3.2.1.3 Carbon Monoxide

A. Principles Involved

The same considerations advanced for SO_2 are also applicable to CO. Chromatographic studies on carbon monoxide and an extensive bibliography on its analytical methods in general are available (Refs. 1-7). Of the different adsorbents that have been studied in the chromatographic analysis of CO, we suggest the use of 30-60 mesh Molecular Sieve 13X (Ref. 3). We are suggesting this adsorbent since it was successfully used in the gas chromatography of CO at 25°C and the material is available commercially.

B. Physical Characteristics

The maximum calibration output requirements for CO can be 50 times those of SO_2, thus requiring 18.0 cm^3 (0.8 mmol) of absorbed CO. A conservative molecular sieve monolayer equivalent area is 500 m^2/g. The area of a CO molecule in the formation of a monomolecular layer is 16.8 $\AA^2$ (Ref. 2).

The 0.8 mmol of CO corresponds to 4.8×10^{20} molecules which would be expected to form a nomomolecular layer of about 80.6 m^2 area. Thus, a gram of the molecular sieve would provide a surface area in excess of that required by 0.8 mmol of CO to form a monomolecular layer. The sorption capacity and kinetic data are not available for this system.

Stainless steel is proposed as the material to be used in the fabrication of the tube. The bulk density of Molecular Sieve 13X is 0.61. Thus, a tube 1 cm in diameter x 3 cm long would have a sufficient volume to hold the absorbent. The weight and size of the entire unit would still be the same as that of the SO_2 unit.

C. Operational Requirements

Same as those for sulfur dioxide except that the unit can be operated at room temperature.

D. Maintenance Requirements

Same as those for sulfur dioxide.

E. Shipping Requirements

Same as those for sulfur dioxide.

F. Estimated Accuracy

Same as that for sulfur dioxide.

G. Estimated Cost

1) Development - $35,000.
2) Production - Unit cost of $25 and set-up cost of approximately $2,000.

H. Advantages/Disadvantages

Same as those for sulfur dioxide and nitrogen dioxide.

I. Design Sketch

Same as that for sulfur dioxide.

J. Recommendations

Determine experimentally the possibility of continuous doping prior to development effort.

K. References

1. Kyriacos, G., and C. E. Boord. Anal. Chem 29:787 (1957).

2. Greene, S. A. Anal. Chem. 31:480 (1958).

3. Trowell, J. M. Anal. Chem. 37:1152 (1965).

4. Wilhite, W. F., and O. L. Hollis. J. Gas Chromat. 6:84 (1968).

5. Altshuller, A. P., S. L. Kopszynski, W. A. Lonneman, T. L. Becker, and R. Slater. Environ. Sci. Technol. 1:899 (1967).

6. Dubois, L., A. Zdrojewski, and J. L. Monkman. J. Air Pollution Control Assoc. 16:135 (1966).

7. Cooper, A. G., Carbon Monoxide. A Bibliography with Abstracts. Washington, D.C HEW, PHS, 1966.

3.2.1.4 Ozone

A. Principles Involved

Ozone has been separated from oxygen by adsorption on refrigerated silica gel, followed by desorption, either in pure form at reduced pressure, or diluted by air, nitrogen, argon, or other gas not strongly adsorbed on silica gel. This is a practical method free from hazards when correctly performed. A pilot plant has been operated successfully to demonstrate the removal of ozone from oxygen and its transfer to other gases, using the silica gel adsorption/desorption technique (Ref. 1).

When the quantities of ozone adsorbed do not have to be large, adsorption can be conducted at room temperature. The adsorption isotherms at 0° and 25°C for ozone in oxygen on a silica gel are shown in Figure 3.2 (the partial pressure of ozone is 10.3 torr when the ozone-oxygen mixture is at atmospheric pressure.

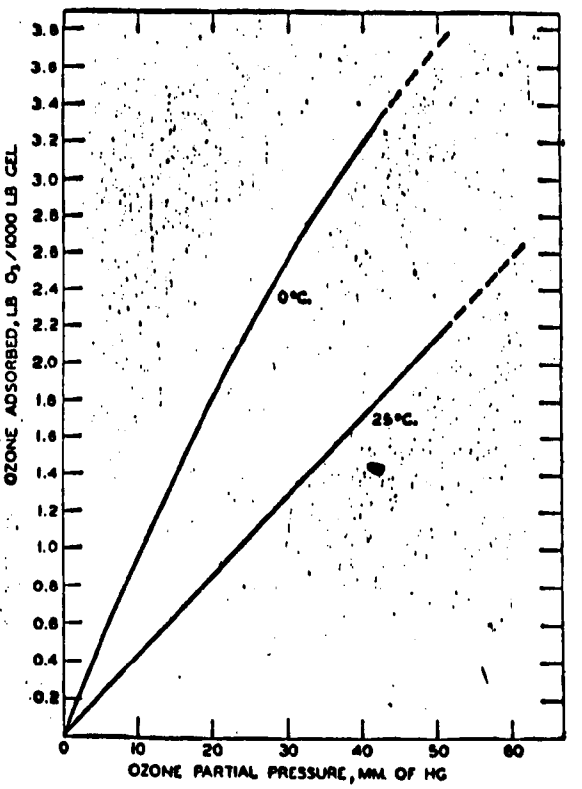


Figure 3-2: Adsorption isotherms at 0° and 25°C for ozone in oxygen on Davison silica gel.

Both small- and large-scale safety tests have been made on silica gel loaded with adsorbed ozone. With up to 9 g of ozone per 100 g of silica gel, no explosion could be initiated at -78°C by an ignited iron wire imbedded in the gel.

Stability of small amounts of silica adsorbed ozone (monomolecular layer) does not appear to have been investigated. The stability of large amounts of adsorbed ozone (4.5 k.g and more per 45.5 kg of silica gel) is determined by the temperature at which it is kept since the decomposition appears to be due only to that of the gas phase ozone. Thus, at -78°C about 9% of ozone had decomposed in 2 weeks while at liquid nitrogen temperature no decomposition was expected. However, ozone adsorbed only to the extent of a monomolecular layer converage would have a very low vapor

pressure and consequently improved stability. Furthermore, no studies appear to have been reported in the literature on other adsorbents for ozone and, thus, this area needs exploration.

B. Physical Characteristics

The maximum calibration output requirements for ozone are the same as those for SO_2, thus requiring 0.36 cm^3 (0.016 mmol) of adsorbed ozone. Using the adsorption isotherms given in Ref. 1, one can calculate that 1 g of the commercial grade silica gel Grade 40 will adsorb 0.008 mmol of ozone at 25°C. Thus, 2 g of such a silica gel would be sufficient to adsorb the required 0.016 mmol of ozone. Although no mention was made whether this was a monolayer adsorbed O_3 or not, it is possible that it was more than a monolayer adsorbed O_3. On the basis of general adsorption characteristics of silica gel considerations, we estimate that probably 2 to 3 times of the above calculated amount of silica gel would be required for the monolayer adsorption. No sorption kinetic data are available on monolayer adsorbed ozone; thus, the feasibility of continuous delivery of ozone still needs to be established.

A glass tube of 1 cm diameter x 7 cm long would be sufficient to pack the required amount of silica gel as indicated above. The weight and size of the entire unit would be the same as that of the SO_2 unit.

C. Operational Requirements

If a continuous delivery of O_3 were found to be feasible, its desorption would be accomplished by a purge gas (nitrogen, for example) stripping at room temperature. The operation would simply consist of a precision valve adjustment on the compressed nitrogen cylinder.

D. Maintenance Requirements

Maintaining the tubes at room temperature or preferably below.

E. Shipping Requirements -

No special shipping requirements besides adequate packing to guard against breakage.

F. Estimated Accuracy

Needs to be established; in principle, as good as the technique for adsorbing ozone on the gel.

G. Estimated Cost

1) Development - $45,000.

2) Production - Source cost of $40 and setup costs of $2,000.

H. Advantages/Disadvantages

Generation of stable and reproducible concentrations of ozone may be possible requiring no skilled personnel in the operation.

I. Design Sketch

Same as that for SO_2 unit.

J. Recommendations

Undertake monomolecular layer adsorbed ozone stability studies.

K. References

1. Cook, G. A., A. D. Kiffer, C. V. Klumpp, A. H. Malik, and L. A. Spence. Advances in Chemistry Series, No. 21. Washington, D.C., American Chemical Society, 1959, p.44.

3.2.1.5 Butene-1

A. Principles Involved

Probably more different adsorbents have been used for hydrocarbon gas chromatographic analysis than for any other class of materials. Among the many references in this field, a number deal directly with the C_4 hydrocarbon analysis:

1) silica gel (Refs. 1-3)

2) modified silica gel and alumina with β, β'-oxydipropionitrile with 20 M carbowax (Ref. 5) with dibenzyl ether (Ref. 6)
3) partially graphitized carbon coated with glycerol (Ref. 7)
4) dimethyl sulfoxide on 60- to 80-mesh Gas Chrom RZ (Ref. 8)
5) activated coconut shell carbon (Type JD-1) (Ref. 9)

By selection of appropriately modified silica gel or alumina, for example, it is claimed that separation of various butene isomers is possible. We propose the use of a 20 M carbowax modified activated alumina adsorbent (Ref. 5). This adsorbent has been used successfully at ambient temperatures in the analysis of C_4 hydrocarbons of concentrations as low as 0.004 ppm and the materials are commercially available.

B. Physical Characteristics

The maximum calibration output requirement for butene-1 is the same as that for NO_2, thus requiring 1.80 cm^3 (0.08 mmol) of adsorbed butene-1. Neither the sorption capacity nor kinetic data are available for this system.

Stainless steel is proposed as the material for the fabrication of the tube. The same tube and entire unit dimensional considerations as for the SO_2 unit apply.

C. Operational Requirements

Same as those for sulfur dioxide.

D. Maintenance Requirements

Same as those for sulfur dioxide.

E. Shipping Requirements

Same as those for sulfur dioxide.

F. Estimated Accuracy

Same as those for sulfur dioxide.

G. Estimated Cost

Same as for sulfur dioxide.

H. Advantages/Disadvantages

Same as for sulfur dioxide, nitrogen dioxide, and carbon monoxide.

I. Design Sketch

Same as that for SO_2.

J. Recommendation

Determine experimentally the feasibility of continuous doping prior to development effort.

K. References

1. Bellar, T. A., and J. E. Sigsby. 151st American Chemical Society National Meeting, Pittsburgh, Pa., March 22-31, 1966.

2. Bruk, A. I., D. A. Vjakhirev, A. V. Kiselev, Y. S. Nikitin, and N. M. Olefirenko. Neftekhimiya 7:145 (1967).

3. Vyakhirev, D. A., M. V. Zuyeva, and A. I. Bruk. Trudy Khimii Khimicheskoi Teknologii Corky 2:268 (1964).

4. Jeung, E., and H. L. Helwig, Symposium on Air Pollution at the 144th National Meeting, American Chemical Society, Los Angeles, Calif., April 1963.

5. Kuley, C. J. Anal. Chem. 35:1472 (1963).

6. Bellar, T. A., and J. E. Sigsby, Jr. Environ. Sci. Technology 1:242 (1967).

7. DiCorcia, A., D. Fritz, and F. Bruner. Anal. Chem. 42:1500 (1970).

8. Trowell, J. M. Anal. Chem. 37:1152 (1965).

9. Turk, A., J. I. Morow, S. H. Stoldt, and W. Baecht. J. Air Pollution Control Assoc. 16:383 (1966).

3.2.2 Effusion Methods

Effusion is descriptive of the process wherein a gas escapes from a container through a small opening. For the generation of test atmospheres, the container must contain the dopant gas (NO_2, SO_2, O_3, CO, or C_4H_8) either in pure form or in a mixture for dilution with air to obtain a test atmosphere. The factors that will affect the ease and precision in obtaining a test atmosphere include the following:

1) The precision with which a specified mixture can be obtained in a container.
2) The chemical and physical stability of the gas mixture.
3) The precision with which small discharge holes may be obtained and reproduced.
4) The range of operating temperatures.
5) Calibration of the doping rates for different gases and conditions, which will vary with viscosity of the doping mixture.
6) The control of airflow in the test manifold.
7) Dead space in the dispensing arrangement.
8) Pressure variations in the storage container.

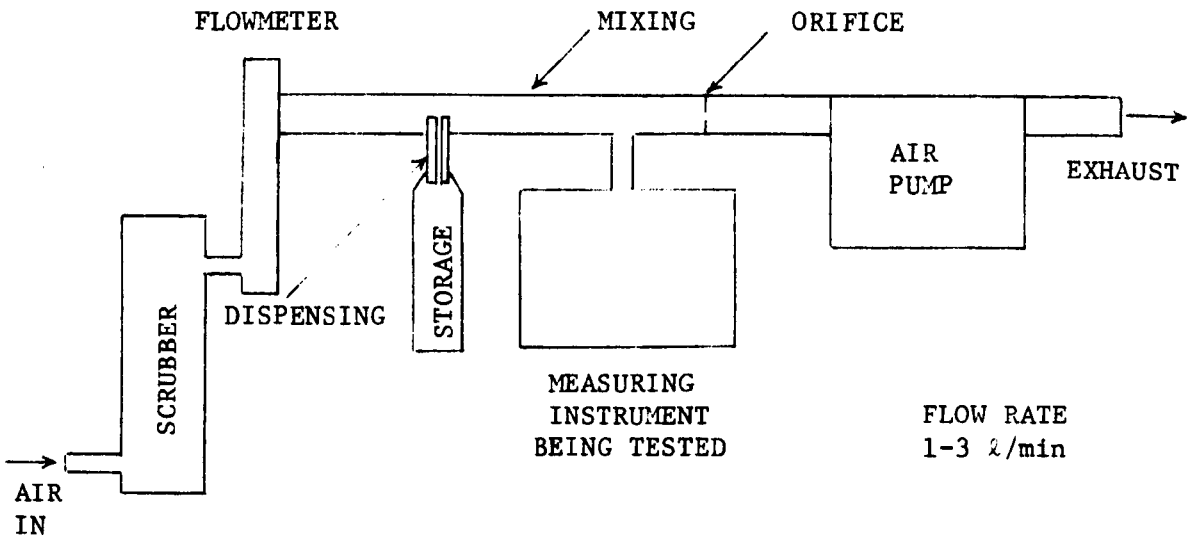
Considering storage, dispensing, and mixing as the three steps in obtaining test atmospheres by effusion, storage is discussed first. In its simplest form, storage consists of a container filled with the gas or with a noninteractive mixture containing the gas. Examples include low pressure cans and high pressure cylinders or lecture bottles. More complex storage systems may involve condensed storage either as an adsorbate or as a liquid as well as storage in other chemical species to be released as needed by reaction. When considering test atmosphere generation by effusion, the

maintenance of a storage pressure in excess of atmospheric pressure is required. Each of the above storage mechanisms is compatible with this requirement. Since the pressure in the storage container affects the dispensing rate, it is necessary to take such pressure changes into account, to maintain a constant pressure, or to provide sufficient storage so that pressure changes little with use.

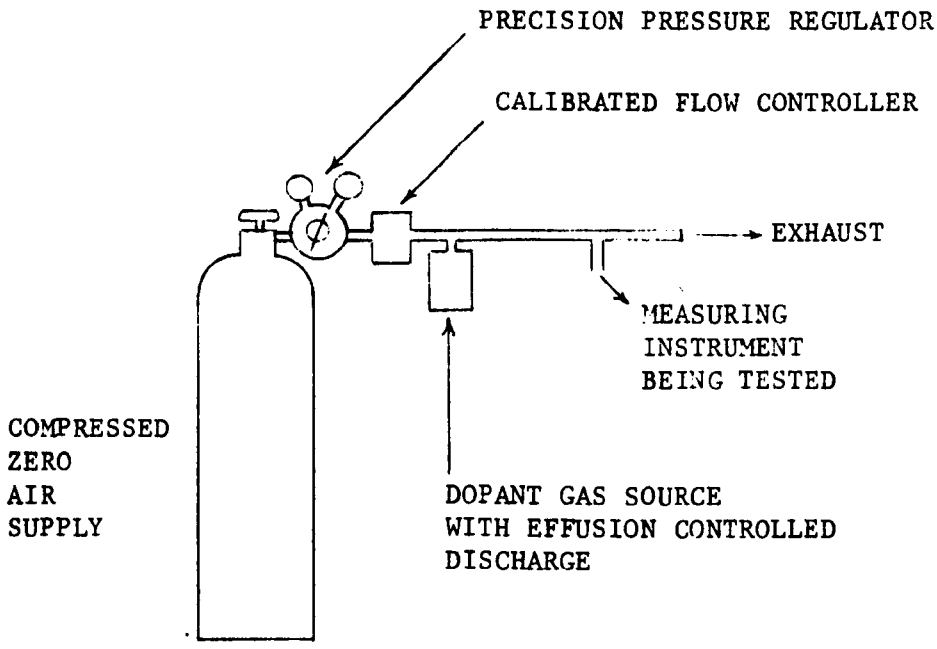
The temperature effect on storage pressure must be taken into account. Although, for a compressed gas at constant volume, pressure is linearly dependent on absolute temperature, the actual number of molecules per unit volume remains constant. Thus, if the dispensing rate is also a linear function of pressure, the rate at which the dopant gas is supplied to a manifold will remain constant, if measured in terms of number of molecules or mass per unit time.

Stability of gas mixtures in a storage container is important in determining accuracy of the test atmosphere generator. The five gases--sulfur dioxide, carbon monoxide, nitrogen dioxide, ozone, and 1-butene--are available commercially in cylinders, the first three in pure form or in gas mixtures while ozone is provided in a cold condensed gas mixture and butene-1 is a liquid at the storage pressure. This and other information indicate that stability in storage is possible but must be examined carefully for each gas in order to determine applicable conditions and duration.

Leaving the dispensing step until last, because it involves diffusion, the mixing of gases in a manifold or a holding volume is the third step in obtaining test atmospheres. Considering only the dynamic process involving a manifold as shown in Figure 3-3(A), this consists of a flow of clean air through a tube that provides taps for a monitoring instrument for insertion of a dopant gas to create a test atmosphere. Assuming that the effusion rate from the dopant source is known, then the accuracy achieved in the dopant content of the test atmosphere depends on control of the manifold flow rate. Manifold flow is maintained with an air pump or blower on the discharge end of the manifold or with a compressed air supply at the input



(A)



(B)

Figure 3-3. Test atmosphere generator.

end (see Figure 3-3(B). Flow can be controlled by means of a critical orifice that will maintain constant volume flow with variable pressure at the low pressure side of the orifice.

The interface between the mixing manifold and storage volume is the dispensing rate control device--in this discussion only effusion methods are being considered. Since all effusion devices depend on flow from high pressure storage to a low pressure manifold through a small channel that restricts the flow to some predetermined rate, the variety of effusion sources are limited although any one basic type may be implemented in a variety of ways. Representative implementations include:

1) A fixed orifice or capillary flow controller to obtain a continuous constant volumetric flow rate from essentially constant pressure sources, disposable storage, and dispenser.
2) Similar to 1) above, but with on-off capability to provide longer useful life.
3) Similar to 2) above, but with adjustable effusion rate.
4) Compressed lecture bottle sources with conventional regulations and flowmeters operative for any gas or dopant level.

Each of these techniques is applicable to various of the dopant pollutant gases. However, they are discussed in the following subsections in terms of a particular pollutant.

3.2.2.1 Sulfur Dioxide

A. Principles Involved

The method described in this section provides for a low pressure pollutant gas source, maintained at almost constant pressure, and with a continuous constant effusion rate, referred to as CLOPES (Constant Low Pressure Effusion Source).

This method requires the pollutant gas to be supplied in low pressure cans, similar to aerosol consumer products, in which the pressure is

maintained by inserting in the can a collapsed plastic bag containing condensed Freon. The supply pressure is thus maintained at the Freon vapor pressure level until the contents of the can are exhausted. The plastic bag prevents dilution of the pollutant gas with Freon.

Dispensing is controlled by a plastic capillary tube on the top of the can. In use the source is activated by breaking off the tip of the plastic capillary allowing gas to effuse from the capillary at a continuous constant rate until exhausted.

B. Physical Characteristics

A 500 cm^3 can containing a pure pollutant gas will supply sufficient pollutant to provide a 50 ppm test atmosphere at a 3 ℓ/min rate for approximately 5000 hours. This number will be reduced proportionally if dilute gas mixtures are employed to provide a large leak rate.

Approximate calculations using the Poiseuille equation for flow indicate that for capillaries of 0.1 mm inside radius, the dopant gas must be in a dilute mixture on the order of 0.1 to 1 percent pollutant to obtain the required test atmospheres. This will reduce the useful life of the source to between 5 and 50 hours which is in excess of that required.

The weight of the "canned gas" should be on the order of 0.5 kg, and its dimensions would be those of an aerosol paint can. It requires the use of a mixing manifold similar to those shown in Figure 3-2.

C. Operational Requirements

A facility is required for fabricating and filling the cans with gas. User requirements are minimal.

D. Maintenance Requirements

The only required maintenance is that associated with the mixing manifolds.

E. Shipping Requirements

Mailable can.

F. Estimated Accuracy

Dependent on pressure variations of Freon with variations in ambient temperature, calibration accuracy of capillary, mixing manifold flow rate, and supply gas mixture. Ten percent should be achievable.

G. Costs

Use cost is highly dependent on volume requirements. If thousands of cans are required, cost per can should be under $5. Development costs are estimated to be approximately $50,000.

H. Advantages/Disadvantages

Once operational, this method provides a minimum cost, minimum effort capability for a large number of users and is adaptable to various gases.

The prime disadvantage is the startup costs. There is an additional problem in determining when the source is exhausted.

I. Design Sketch

See Figure 3-4.

J. Recommendations

This should be given serious consideration for providing test atmospheres.

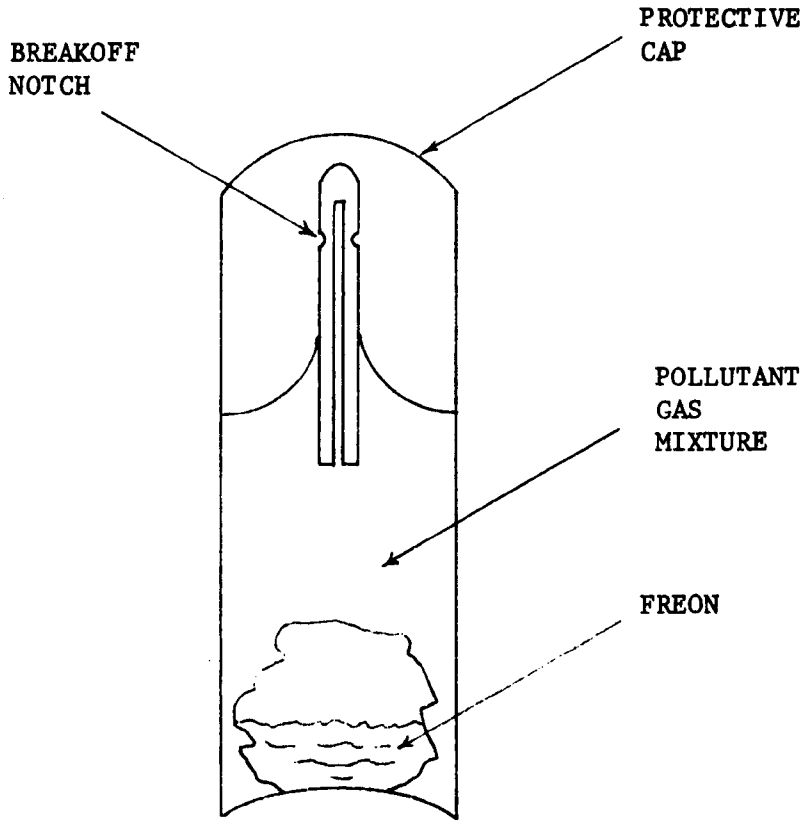


Figure 3-4. Constant low pressure effusion source.

3.2.2.2 Nitrogen Dioxide

A. Principles Involved

In order to increase the useful life of the pollutant source described in Section 3.2.2.1, it may be provided with an on-off capability.

Any on-off valve used in a low flow rate line must not introduce dead space. At a flow rate of 0.003 cm^3/min such as required for 1 ppm doping of a 3 ℓ/min gas stream, a dead space of 1 cm^3 would require over 16 hours to flush. At these flow rates, it is also difficult to discern when there is flow; i.e., a valve that is stuck closed would be almost undetectable.

B. Physical Characteristics

Two methods are suggested, one of which is to plug the capillary with a needle and the other is to energize a heater to allow gas to form. In the first case, the capillary discharge tube would be capped with a solenoid-operated needle which, when unenergized, plugs the end of the capillary. With current in the solenoid, the needle is withdrawn and gas flows. A sketch of this is shown in Section I (Figure 3-5(A)..

In the second example, a metal capillary discharge tube is employed but it is plugged with a rod of a lower thermal expansion material at the discharge end. Heat applied through a small coil would be sufficient to expand the capillary relative to the plug allowing gas to flow in the space thus provided as shown in Section I (Figure 3-5(B).

In neither instance will more than a few ounces be added to the weight, and a negligible dimensional change will be entailed.

C. Operational Requirements

Same as in Section 2.1 except for small amount of electrical power.

D. Maintenance Requirement

No additional maintenance required.

E. Shipping Requirements

Same as for the CLOPES.

F. Estimated Accuracy

Same as for the CLOPES source.

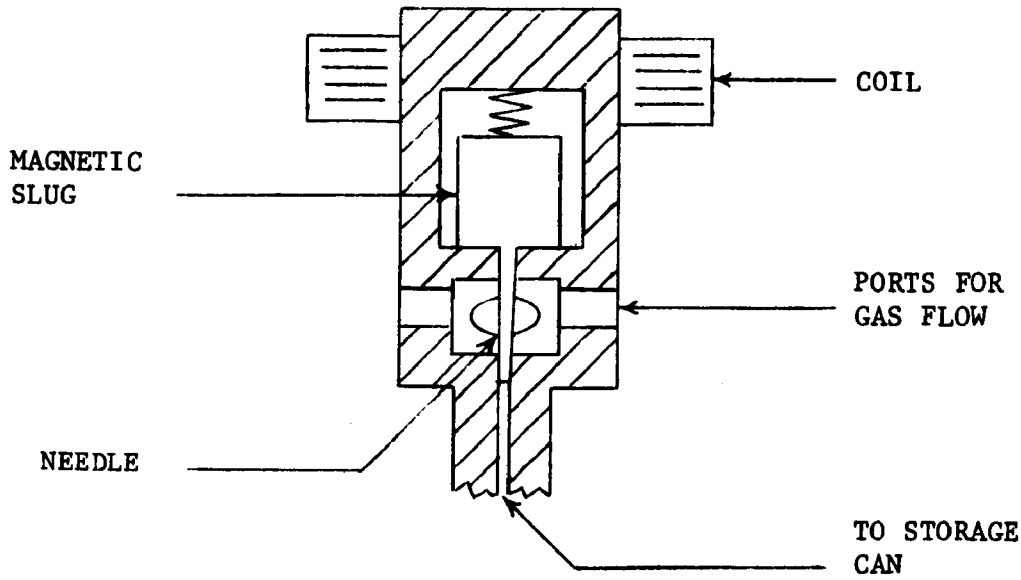
G. Costs

Additional $1 per can estimated over the CLOPES source in volume usage. Little additional development costs.

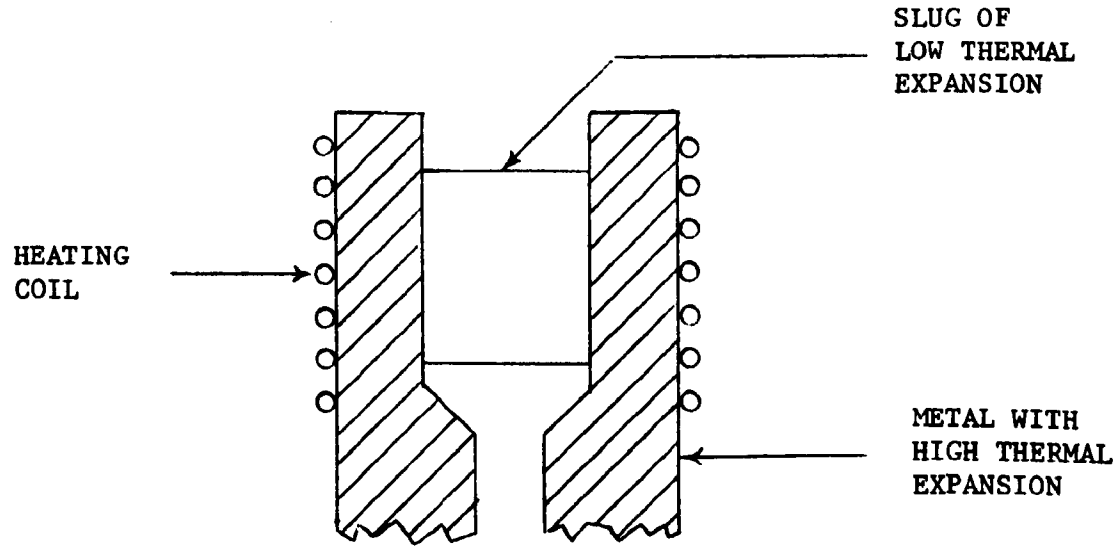
H. Advantages/Disadvantages

Additional useful life due to on-off capability. Otherwise same as for the CLOPES source.

I. Design Sketch



(A) Solenoid-operated needle valve (closed position)



(B) Thermally operated valve

Figure 3-5. On-off valves for CLOPES source.

J. Recommendations

On the basis of present data, the on-off feature does not appear to be required. However, the simple plug cut-off will increase the useful life by a large factor and may be cost-effective.

3.2.2.3 Carbon Monoxide

A. Principle Involved

This method provides for a storage arrangement similar to the CLOPES source except that the Freon is omitted from the storage volume, and an adjustable metering valve is used at the output.

A can similar to that in Figure 3-4 is filled to a specified pressure with the appropriate pollutant mixture but without Freon so as to illustrate the case with a variable storage pressure. Various precision valves are available. Valves with sapphire seats made for vacuum applications can be controlled to as low as 10^{-11} ℓ/min with one atmosphere across them while relatively inexpensive needle valves have maximum flow rates of 0.5 ℓ/min but are controllable to 5×10^{-3} ℓ/min or less.

Since it is obvious that almost any flow rate one desires can be obtained but at a rapidly increasing cost for lower flow rates, the high flow rate valve will be considered. At 5×10^{-3} ℓ/min, it is necessary to have a pollutant concentration of about 1000 ppm in the storage volume to obtain 5 ppm in a gas stream flow at 1 ℓ/min. At this rate 0.3ℓ at a pressure of 1 atmosphere will be used each hour. If a 1-ℓ storage volume is at a pressure of 3 atmospheres initially, after 1 hour the storage pressure will be reduced to 2.7 atmospheres with a consequent reduction in flow rate to 4.5×10^{-3} ℓ/min. If no correction is provided, this introduces an error of 10 percent in the pollutant concentration in the test atmosphere. If, however, a controlled flow rate of 5×10^{-4} ℓ/min is obtainable, then the error becomes 1 percent. The viability of this method thus depends on the availability of a low flow-rate valve at an acceptable cost.

B. Physical Characteristics

The storage unit is a lightweight can with a 1-ℓ capacity with a valve assembly mounted on the top. The valve assembly has a screwdriver locked metering valve and a toggle on-off valve (see Figure 3-6).

The overall weight of the unit is 0.9 kg, its dimensions are about 7.6 cm o.d. by 20.3 cm high. The cans are reusable.

C. Operational Requirements

The canned gas is attached to a controlled source of clean air and its output is attached directly to the instrument manifold. The airflow is started and the toggle valve is opened 60 s before a reading is taken in order to flush the valve assembly.

D. Maintenance Requirements

Because of the cost of the valve, the assembly is returned to the issuing organization for refilling and adjustment of the metering valve. Metering valves are calibrated volumetrically by displacement of a liquid.

E. Shipping Requirements

Capability to ship a 0.9 kg can. A clean air supply is required at the test site.

F. Estimated Accuracy

Ten-percent accuracy should be readily obtainable.

G. Estimated Costs

A realistic cost for identifying and characterizing an optimum system should be about $50,000. Once established, the actual costs of each valve/container assembly should be of the order of $100 and refilling should be accomplished at no more than $10.

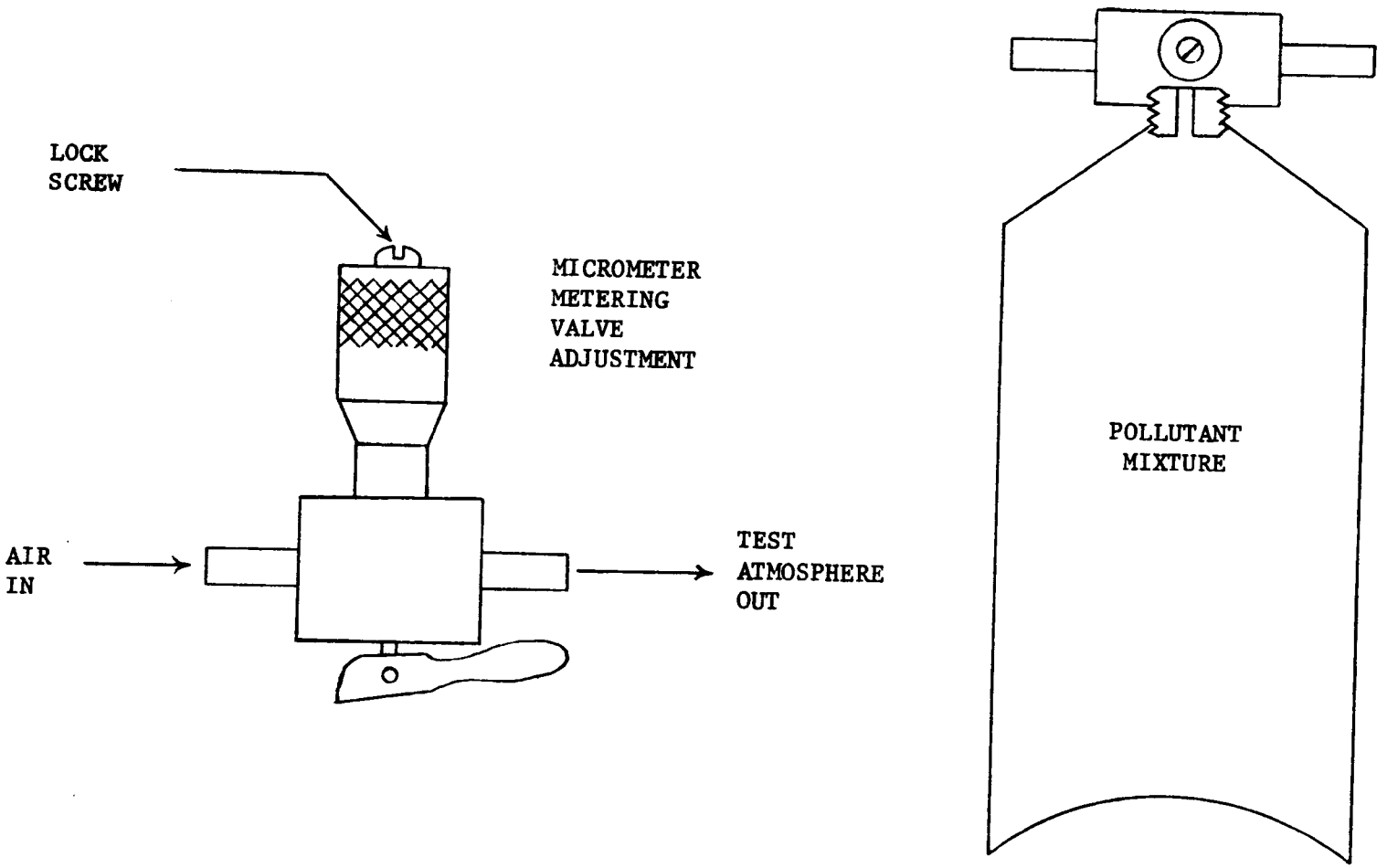


Figure 3-6. Storage unit with metering valve.

H. Advantages/Disadvantages

The requirement for reuse of the test atmosphere generator is a disadvantage over some other methods. The requirement for a controlled flow of clean air is common to most methods. The low shipping weight and relative ease of use is a definite advantage.

I. Design Sketch

See Figure 3-6.

J. Recommendations

This should be compared to throw-away containers in terms of overall cost and effectiveness.

3.2.2.4 Ozone

The primary problem for effusion sources of ozone is that of stability of the ozone in a gas mixture. While there are indications that long-term stability of ozone can be obtained in dilute mixtures and compressed gas mixtures containing ozone are available, these data are not sufficient to serve as the basis of an effusion source. One method that might be feasible is to provide a small source of ultraviolet radiation in a gas mixture containing oxygen. This would provide some equilibrium concentration of ozone in the mixture which would have to be determined. At this time, no data exist on which to base such a method.

In order to ascertain the possibility of a CLOPES source for ozone, the equilibrium ozone concentration in a low pressure can which contains a small ultraviolet radiation source should be determined for various oxygen-containing gas mixtures, materials, and pressures.

3.2.2.5 1-Butene

A. Principles Involved

Butene-1 is a gas at atmospheric pressure, but in storage containers it is a liquid with a vapor pressure at 70°F of 24 lb/in^2 g. Thus, it is ideal for a CLOPES-type source since it will not require a Freon reservoir to maintain a constant storage pressure. In this present method, however, a lecture bottle containing 2.7 ft^3 (28, 317 cm^3) of 1-butene is used.

A lecture bottle of 1-butene is provided with a regulator to give a delivery pressure of 4 lb/in^2 g. This is coupled to the instrument manifold through a fine metering valve (Nupro "5" series cross-pattern metering valve, for example) to give a flow rate of 10^{-3} cm^3/min. At these rates, direct insertion in a manifold in which a flow rate of 1 ℓ/min is maintained will give a concentration of 1 ppm. Dead space in the plumbing must be at a minimum. The valve may be preset to give "blind" detection levels.

B. Physical Characteristics

The weight of this apparatus approximates 4.5 kg and its dimensions are of the order of 5.1 by 50.8 cm. It consists of a small gas cylinder with a regulator and valve assembly connected directly to the instrument manifold as shown in Figure 3-7.

C. Operation Characteristics

The metering valve would be preset to a specific flow rate for a given inlet pressure. Operation consists of attaching the lecture bottle and valve assembly to the manifold and adjusting the regulator to the specified inlet pressure with a specified flow rate for air in the manifold.

D. Maintenance Requirements

Only a minimum of maintenance is required. Lecture bottles of gas are available commercially.

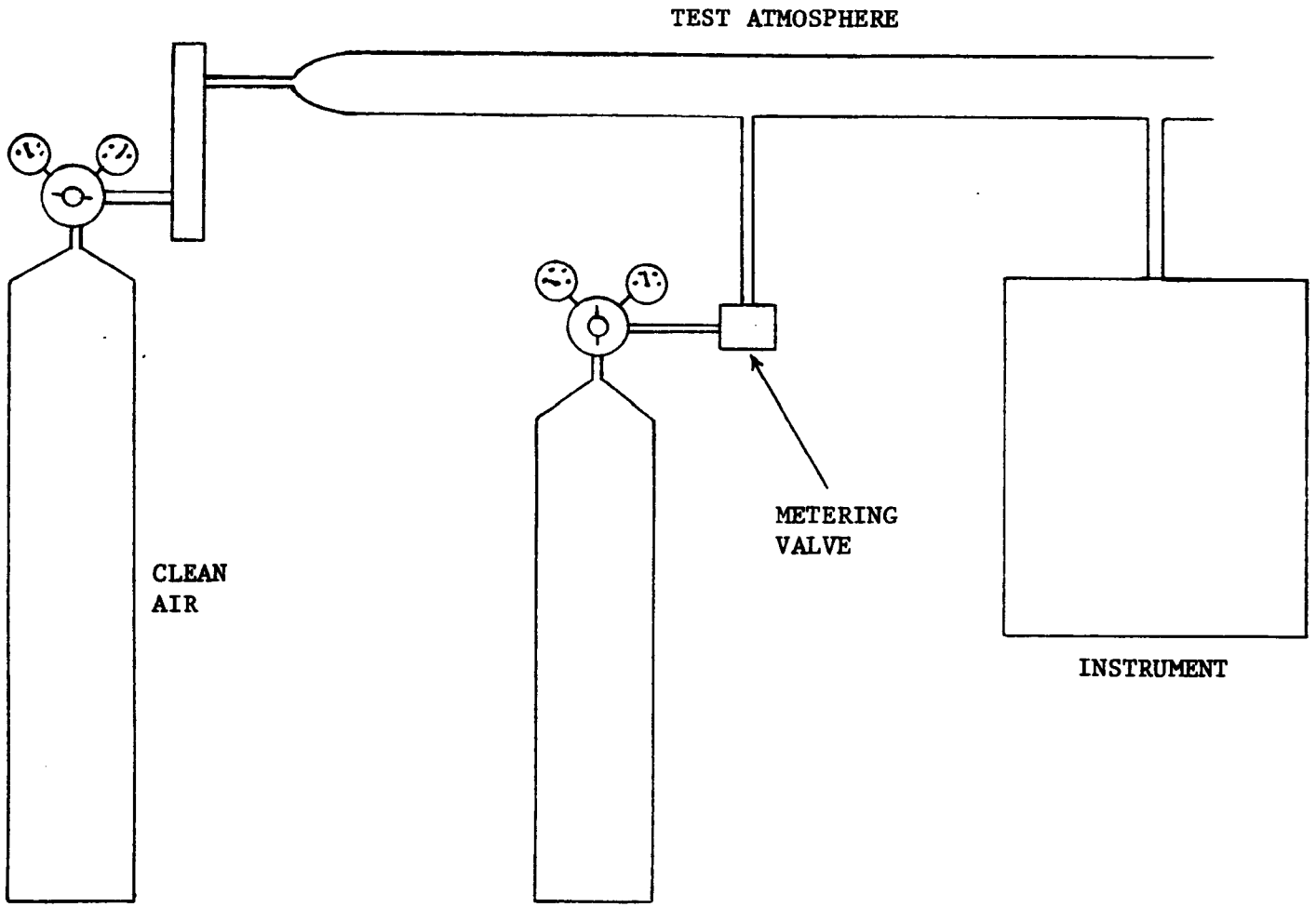


Figure 3-7. Test generator with metering valve.

E. Shipping Requirements

The shipping assembly will weigh about 5.5 kg and will require return. The unit is reusable a large number of times.

F. Estimated Accuracy

The direct introduction of undiluted pollutant air into an airstream requires accurate control of flow rates that are difficult to maintain. It is estimated that ± 20% is the best accuracy that is possible in a practical environment.

G. Estimated Costs

The valve and cylinder assemblies may cost $200 each but refilling and regeneration, after 100 uses, is only about $10. Development cost to prove the system out should be less than $30,000.

H. Advantages/Disadvantages

This method is relatively easy to implement and components are commercially available. It may not be possible to obtain sufficient accuracy but since components are common, personnel may be trained to use them with a minimum effort.

I. Design Sketch. See Figure 3-7.

J. Recommendations

Since this utilizes standard components and techniques, it may serve as a baseline for comparison of other potential methods in the evaluation.

3.2.3 Thin Film Evaporation

Thin films may be either gaseous, liquid, or solid. A gaseous thin film is formed by adsorption on a solid surface and is released by desorption. This process for generation of test atmospheres is considered in Section 3.2.1. A solid thin film may be prepared for the pollutant gases

of interest but this requires cumbersome refrigeration techniques that are impractical for field applications. Liquid films may be used for test atmosphere generation but the pure pollutants would also require either refrigeration or high pressures to maintain them in a liquid state. However, the pollutants may be dissolved in various solvents and thin liquid films of the solutions employed as controlled pollutant sources for test atmosphere generation.

In chemical engineering, solvents are routinely employed in adsorption or contact columns for removal of components from gas streams. The reverse process (i.e., injection of a gas into a gas stream by release from solution) is an equally viable process. The solution containing the pollutant gas must be maintained in a sealed container until use since it will release the solute in order to attain equilibrium with the atmosphere above it. In use, the solution is exposed to a flowing airstream and a steady state is achieved between solution flow, airflow, and rate of outgassing since there is insufficient pollutant to achieve equilibrium with the airstream. A thin liquid film of solution is employed to achieve a rapid rate of outgassing. The concentration in the airstream will thus depend on:

1) Airflow rate
2) Concentration of solute in solution
3) Solution flow rate.

A schematic representation of a test atmosphere generation system employing thin films of pollutant gas solutions is shown in Figure 3-8.

An inert collapsible bag containing the solution is maintained at a known height to give a constant rate of flow of solution through a capillary to the column. In the column, a thin liquid film flows over the glass beads and out the bottom. An airstream flows up through the column and, after condensation of any solvent vapors, constitutes the test atmosphere.

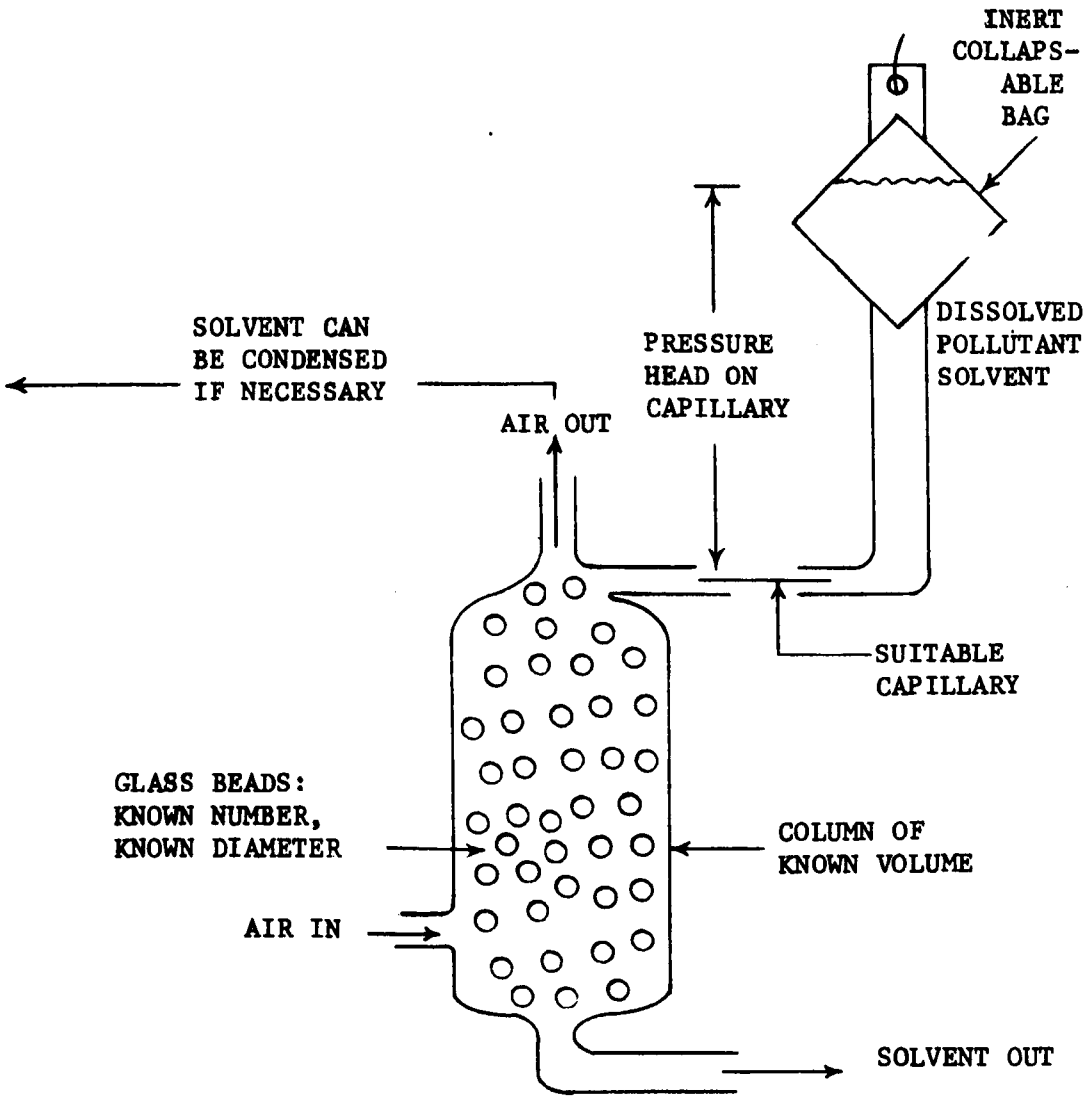


Figure 3-8. Contact column test generator.

The quantity of liquid flowing through the capillary with a moderate pressure head is determined by Poiseville's law (Ref. 1)

$$q = \pi p r^4 / 8 \ell \eta$$

where

q = flow rate, cm^3/s

p = differential pressure, dyn/cm^2

r = capillary radius, cm

ℓ = capillary length, cm

η = liquid viscosity, poise ($dyn\text{-}s/cm^2$).

The column length must be sufficient to essentially complete stripping of the solute pollutant from the liquid film. The amount of solute from the solvent can be estimated from the relationship

$$\Delta C = C_o - C = C_o \left[1 - \exp \frac{kAk't}{V}\right]$$

where

ΔC = concentration loss per unit volume of solution at any time, t

C = concentration of solute in solution at any time

C_o = initial concentration of solution

k = 2.5×10^{-4} mol min/cm^2/atm specific rate of release (estimated for a system of this general size from standard j-factor versus Reynolds number correlations (Ref. 2)

A = surface area of film of solution

$k' = \dfrac{\Delta P \text{ in atmospheres}}{\Delta C \text{ in same units as } C \text{ and } C_o}$

V = volume of liquid, and

t = time in minutes since solution was introduced into column.

The rate of pollutant introduction into the gas stream is thus given by ΔC times the volumetric flow rate of solution through the column. In actual

practice, this is an upper limit to the rate of introduction but for a given column and set of conditions, the actual rate would be a reproducible function of this maximum rate.

The use of thin film evaporation for the generation of test atmospheres is thus based on the release of dissolved pollutants from thin films of liquids obtained in a column packed with glass beads. Distribution of the solution is from a central laboratory sealed in plastic bags. The column, associated apparatus, and air supply (and possibly a cascade air dilution apparatus), would be required at the test site. Excess test atmospheres must be properly vented.

3.2.3.1 Sulfur Dioxide

A. Principles Involved

A solution of sulfur dioxide in carbon tetrachloride should be suitable.

B. Physical Characteristics

Since 18.45 cm^3 of SO_2 will dissolve in CCL_4 at 25°C and 760 torr (Ref. 3), a more than adequate amount of SO_2 will be available. A dilute solution is therefore required. This may be prepared either by first putting CCl_4 in the plastic container, then adding a gas mixture containing SO_2, or preparing the solution first, then introducing it into the bag and sealing the container.

C. Operational Requirements

Operation should be simple once the apparatus is assembled. In sequence:

1) Liquid flow is turned on by a toggle valve, by opening a clamp, or by opening a regular valve all the way. Flow is controlled by the capillary.
2) Airflow is adjusted to a specified rate.
3) When liquid begins to accumulate in the bottom of the contact column, the instrument to be tested can start sampling the test atmospheres.

4) Care should be taken to maintain the liquid at the preset level to insure constant solution flow.

If the solvent is removed from the airstream by a cold trap, the refrigerant and the trap should be placed in the Dewar flask before the test begins.

D. Maintenance Requirements

The device should be cleaned and checked for correct flows before and after field use. Broken parts should be replaced. The whole system should be calibrated in the home laboratory prior to being used in the field. Solutions of pollutants will have to be prepared and analyzed in the home laboratory.

E. Shipping Requirements

For the apparatus, the case should be rigid and the parts should be strapped in. When shipped, the interior should be stuffed with shock absorbant filler of some kind.

The solution of pollutant may be shipped sealed in a plastic bag that is inert to the pollutant. A second material may be sealed around the basic bag container if its permeation characteristics are unfavorable. The bag of test solution should be shipped in a rigid container.

The apparatus, as diagrammed in Figure 3-8, including a cold trap and a Dewar flask, can be contained in a case 61 x 46 x 20 cm in size. The weight of the apparatus less the case should be less than 2.3 kg. A case could be built to weigh about 6.8 kg total.

F. Estimated Accuracy

Delivery of an accurately known concentration of sulfur dioxide will depend on measurements in the central laboratory which relate concentration to the various parameters of the apparatus and to temperature.

Precision of delivery will depend on control of temperature and the accuracy of the hydrostatic head and the airflow setting. A single point

flowmeter can help the latter. The hydrostatic head can be designated by fixed marks on a stick but will require frequent adjustment.

G. Estimated Costs

The provision of plastic bags containing the solution that will serve as the pollutant source is a significant cost advantage. They should require little effort to prepare and should cost less than $5 each.

The apparatus required at the test site will cost approximately $300.

Since this is an unproven method, approximately $35,000 in developmental costs would be required before it is used.

H. Advantages/Disadvantages

With proper quality control, there is no need to rely on outsiders for delivery of a known concentration of sulfur dioxide to the instrument to be tested.

Accuracy and precision should be acceptable.

The only disadvantages might arise from transportation and handling of the solution. If it is not kept enclosed, the dissolved pollutant will escape.

I. Design Sketch

See Figure 3-8.

J. Recommendations

This method should be developed only if some advantage now not apparent can be obtained by using it. It is, however, a reasonable approach.

K. References

1. Weast, R. C., and S. M. Selby (Eds.). Handbook of Chemistry and Physics. 48th Ed. Cleveland, Ohio, Chemical Rubber Co., 1968, p. F-33.

2. Perry, J. H. Chemical Engineer's Handbook. 3rd Ed. N.Y., McGraw-Hill Book Co., 1950, p. 547.

3. Stephen, H., and T. Stephen (Eds.). Solubilities of Inorganic and Organic Compounds. Vol. 1. N.Y., The MacMillan Co., 1963, p.960.

3.2.3.2 Nitrogen Dioxide

A device for generating a test atmosphere on NO_2 would be exactly as described for SO_2. NO_2 will dissolve in a number of substances, including 1,3,5-trioxane (Ref. 1).

The various costs could also be essentially the same as for SO_2.

References

1. Stephens, H., and T. Stephens (Eds.). Solubilities of Inorganic and Organic Compounds. Vol. I. N.Y., MacMillan and Co., 1963, pp. 922-925.

3.2.3.3 Carbon Monoxide

A test atmosphere of CO can be generated in virtually the same manner as the test atmosphere for SO_2. Carbon monoxide is soluble in a number of solvents including chloroxane and acetone (Ref. 1).

References

1. Stephens, H., and T. Stephens (Eds.).Solubilities of Inorganic and Organic Compounds. Vol. I. N.Y., MacMillan and Co., 1963, pp. 1052-1053.

3.2.3.4 Ozone

Ozone would have to be generated in the laboratory. A concentration of about 1 percent O_3 can be generated with commercial ozonizers. In contact with liquid CCl_4, 0.03 cm^3 gaseous O_3 will dissolve per cm^3 of CCl_4 (Ref. 1). At flow rates of 1 cm^3/min solution and 1ℓ/min air, O_3 will be delivered to the airstream at an estimated 0.002 cm^3/min.

The cost of the O_3 device should be increased by about $250 over that for SO_2 to cover the price of a suitable O_3 generator.

References

1. Stephens, H. and T. Stephens (Eds.). Solubilities of Inorganic and Organic Compounds. Vol. I. N.Y., MacMillan and Co., 1963, p. 576.

3.2.3.5 Butene-1

Butene-1 could be dispensed in the same manner as SO_2. Butene-1 is soluble in a number of solvents to which the flame ionization detector does not respond (e.g., CCl_4). For generation of test atmospheres for hydrocarbons, evaporation of a liquid hydrocarbon such as n-hexane might be better than the use of a solution of Butene-1.

3.2.4 Novel Permeation Methods

Permeation tubes for the preparation of known concentration of air pollutants were originally suggested by O'Keefe and Ortman (Ref. 1); since then the performance characteristics of such tubes (Ref. 2) and their critical evaluation for sulfur dioxide (Ref. 3) have been reported.

Permeation tubes offer a convenient and relatively simple means of conducting dynamic calibration of gas detection devices. However, accurate and precise temperature control is essential in prcducing exact sample emission rates. Depending upon the sample gas involved, the temperature change, and the permeation material and wall thickness, steady-state operation of a permeation tube may require equilibrium saturation times of anywhere from 2 to over a 100 hours. This places a severe limitation on the utility of permeation tubes since it is impractical to wait for many hours for the tube emission rate to stabilize after only moderate temperature changes.

Although precalibrated permeation tubes are obtainable from commercial sources, the following practical drawbacks have been experienced with them: (Ref. 2 and 4)

1) Tubes, which are sealed with balls of glass or stainless steel, may leak;
2) The permeating gas may be contaminated with solid particles and/or water;
3) Water may permeate into the tube during storage and shipping;
4) The permeation rate for NO_2 in a single-walled tube is inconveniently high;

5) The thicker the tube wall, the longer the equilibrium saturation time;
6) If the tube wall thickness is not sufficient, dimensional tube changes occur which in turn affect permeation rate;
7) When liquid phase permeant is in contact with the area of permeation, the permeation rate is affected; and
8) Accumulation of grease and moisture on tube exterior affect the permeation rate.

We propose a new design for permeation tubes adapted from a recently patented gas sensing device used in the medical field (Ref. 5) which should obviate most if not all of the above mentioned drawbacks. Of all of the problems and drawbacks mentioned, the lost time waiting for the tube emission rate to stabilize is the most serious. Although the equilibrium saturation time is dependent upon a number of factors (including the type of gas and the kind of tube material used), two factors are important for achievement of fast equilibrium saturation regardless of the type of gas and tube material used. These are the operating temperature and the wall thickness. Thus the thinner the wall, the faster the equilibrium saturation is reached. Our proposal provides for these two factors.

For the case of gaseous penetrants that are sparingly soluble in the membrane substance, and that do not chemically associate with one another or the membrane material, the membrane molecular structure is not perturbed by the dissolved molecules. Thus, diffusivity of a penetrant is essentially constant throughout the membrane. Moreover, the solubility of such species within the membrane is essentially directly proportional to its activity in the equilibrium gas phase, and Henry's Law applies:

$$c_i = k_i p_i \tag{1}$$

$$J_i = D_i \frac{(c_{i\,(1)} - c_{i\,(2)})}{\ell} \tag{2}$$

or

$$J_i = k_i D_i \frac{(p_{i\,(1)} - p_{i\,(2)})}{\ell} \qquad (3)$$

Where c_i is the concentration of (i) in the surface of the membrane, k_i is the solubility coefficient in the membrane, p_i is the pressure at the surface, J_i is the mass flux (gm/cm^2 s), D_i is the diffusivity (cm^2/s), the subscripts (1) and (2) refer to the "upstream" and "downstream" surfaces of the membrane, and ℓ is the membrane thickness. The product $(k_i D_i)$ is usually termed the "permeability," P_i, of the membrane to (i); it is equal to the flux of (i) through a membrane of unit thickness when exposed to a unit pressure-difference across it. Most gaseous penetrants and membranes obey equation (3); the permeability is thus <u>independent</u> of the total pressure of the penetrating gas.

In the decision on membrane thickness, the following considerations are involved. When gases diffuse through a solid or liquid they take a definite time, the magnitude of which is related to the diffusion rate. If one measures and plots the rise in pressure in a constant volume with time that would result on one side of a membrane from a discontinuous change in pressure on the other at time t = o, and then draws an asymptote to the steady state conditions, the asymptote will cut the time axis at the coordinate τ. This time lag τ is related to D and the thickness of the membrane, ℓ, as follows:

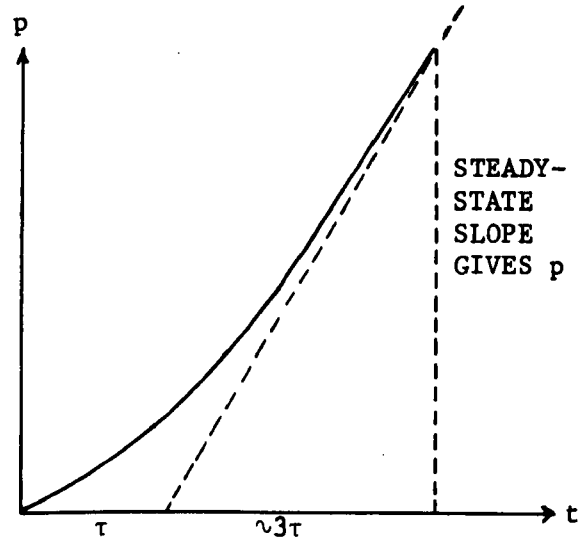
$$\tau = \frac{\ell^2}{6D} .$$

The time to reach a steady state condition is 3τ, as shown in Figure 3-9. For D = 10^{-6} cm^2/s; $\ell = 2.5 \times 10^{-3}$ cm; τ = 1 s. The permeation can be measured in torr-ℓ/s and the following relationship relates all the membrane parameters:

$$p = k_D A \frac{p_1 - p_2}{\ell} t$$

where: A is the membrane area, t is time and the other parameters as defined before.

THE TIME LAG τ



FOR $D = 10^{-6} cm^2/s^{-1}$; $\ell = 2.5 \times 10^{-3} cm$; $\tau = 1$ s

Figure 3-9. Time lag vs pressure curve.

If the permeability constant is expressed in units of cm^3 (STP) cm $(cm^2 s$ cm of Hg$)^{-1}$, then it is found that the permeability constant falls in the range of 10^{-6} to 10^{-13} for most pure polymeric membranes and permeants. A review of the available permeability data permits one to make a further generalization insofar as the different polymers (used as membranes) are concerned. The different classes of polymers may be arranged in the following order of decreasing permeabilities: silicone rubbers > silicone rubber copolymers > hydrocarbon rubbers > nonelastomers. Thus, for example, nitrogen and carbon dioxide permeabilities for polydimethyl siloxane, a silicone rubber, and FEP (fluorinated ethylene/propylene copolymer) compare as follows:

$P \times 10^{10}$ $(cm^3 STP)$ (cm)/$(cm^2$ s cmHg)

	N_2	CO_2
Polydimethyl siloxane	227	355
FEP	1.6	13

Typical values of D reported for silicone rubber are around $10^{-6} cm^2/s$ and for FEP, 10^{-9} cm^2/s, for hydrocarbon permeants.

The permeation device that we are proposing is adapted from the patent of Van der Grinten on a "gas sensing device" (Ref. 5) and is depicted in Figure 3-10 below.

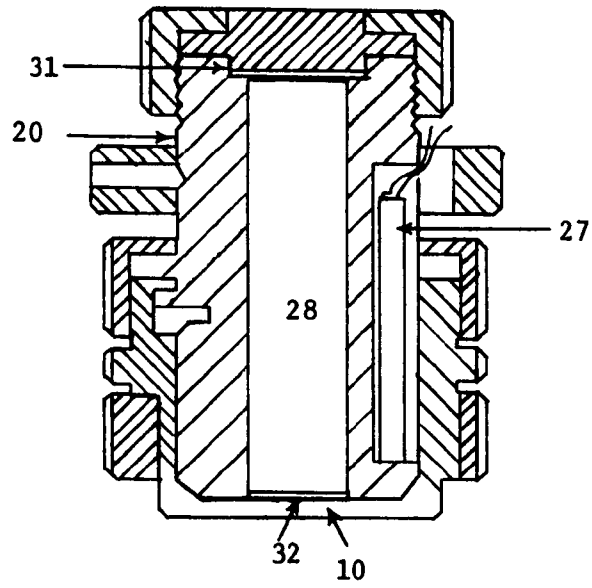


Figure 3-10. Permeation device.

The unit consists of a stainless steel cylinder (28) capped with a screw cap (31) on one end and a discrete blend of a solid polymer in the performations of a perforated metal plate (32), heat pressed to a thin film of a polymer (10), at the other end. Such a membrane in the patented device permitted the maintenance of a 10^{-6} to 10^{-8} torr vacuum in the system over a range of temperatures. Thus, apparently obtaining a pinhole-free membrane was not a problem. The entire unit was operated at a constant temperature, maintained by means of a thermoregulated heater (27). As this device has not been used before in a permeation application that we require, nothing definite can be said about the membrane cross sectional area requirements at this time.

While in all of the permeation tubes designed up to now, one is limited to a certain tube wall thickness below which one cannot go for structural or mechanical strength reasons, the polymer-perforated metal membrane permits much thinner membranes and, as a result, drastically reduces the equilibrium saturation time required for the membrane. In addition, none of the currently designed permeation tubes provide for

operation at isothermal conditions without using isothermal chambers. The proposed device should not require such chambers. Thirdly, current permeation tubes must use nonelastomeric materials as the permeating medium even though they are not ideal with respect to permeability and practicality. The polymer-perforated metal membrane device does not require nonelastomers for the membrane, it can just as satisfactorily use an elastomer as the membrane material. In fact, one of the patented polymeric impregnants was polydimethyl siloxane.

On the basis of the extensive permeability background in our laboratories and some specific recent work in the literature (Ref. 6) polydimethyl siloxane appears to be the best material for use as the membrane material in the perforations of the metal plate. This silicone rubber showed a minimum change in permeability with temperature change (5% for a 10°C increase in temperature) and the permeation rate of the membrane attains 90% of the steady-state value within 10 min., thus eliminating one of the more serious drawbacks of current permeation tubes.

3.2.4.1 Sulfur Dioxide

A. Principles Involved

The calibration output requirements for SO_2 have been specified as 1 ppm as the upper limit with the field usable test atmosphere generating device delivering the doped air at 1 to 3 ℓ/m for periods up to 2 hr. Thus, the maximum flow rate of SO_2 required would be 0.001 to 0.003 cm^3/min which is a several orders of magnitude lower rate than that achievable with a pure polydimethyl siloxane membrane. The use of a polymer-perforated metal composite will have a lower permeability than pure polydimethyl siloxane; however, it would be expected to be in the range required. Furthermore, the permeation rate can be regulated by the membrane area and the temperature at which the device is operated.

B. Physical Characteristics

At the instrument site a supply or source for zero (clean) air is required. This may be either a compressed tank of clean air or an air

scrubbing system. Alternatively, zero air source can be a part of the portable test atmosphere generating unit proposed. For the purposes of setting upper portable unit dimensions the following is suggested:

Total weight: 3.5 kg

- air lecture bottle 2.3 kg
- permeation tube 0.5 kg
- valve + tubing 0.5 kg
- manifold system 0.2 kg

Total dimensions:

- air lecture bottle 38.1 x 5.1 cm. diameter;
- permeation tube 12.7 x 2.5 cm. diameter (estimated - will require experimental confirmation);
- manifold system

C. Operational Requirements

The operation of the unit would consist of plugging in the heater of the permeation tube set to produce the desired temperature and adjusting the precision valve on the compressed air bottle for the desired rate of diluent air delivery which could be directed into the instrument manifold.

D. Maintenance Requirements

Compressed air bottle - none;

Permeation tube - none;

Entire unit requires minimal maintenance.

E. Shipping Requirements

The membrane end of the permeation tube could be fitted with threads and a gastight cover for shipping and storing purposes and when the cover is removed for screwing the tube into the manifold.

F. Estimated Accuracy

Accuracy of the existing permeation tubes is claimed to be as good as ± 2%. The same would be expected for the proposed device.

G. Estimated Cost

1) Development costs of approximately $45,000.

2) Initial Setup Costs

Zero air in cylinder with regulator -	$150
SO_2 in cylinder with regulator	$150
Precision valve	$200
Permeation tubes	$200
Plumbing and bag	$100

3) Operation costs are negligible

H. Advantages/Disadvantages

Known and constant concentrations of gases may be conveniently prepared by using permeation devices. Simple to operate with minimum of support requirements. Can be operated by unskilled personnel with high precision. If replaceable membrane discs are designed into the tube, costs would be minimal.

I. Design Sketch

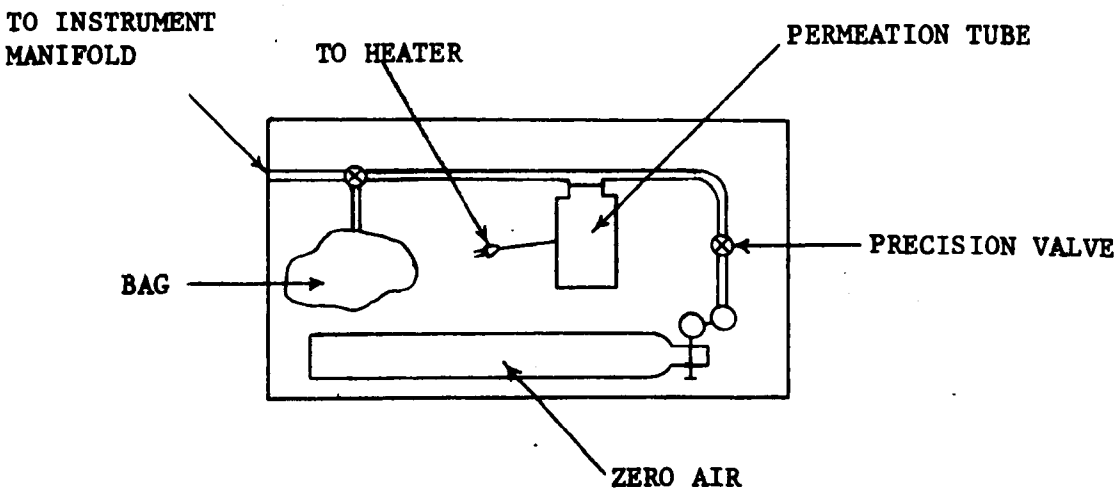


Figure 3-11. Permeation test atmosphere generator.

J. Recommendation

Undertake development of the permeation device.

K. References

1. O'Keeffe, A. E., and G. C. Ortman. Anal. Chem. 38 (6):760 (1966).

2. Lucero, D. P. Anal. Chem. 43 (13):1744 (1971).

3. Scaringelli, F. P., S. A. Frey, and B. E. Saltzman. Amer. Ind. Hyg. Assoc. J. 28:260, 1967.

4. Lindquist, F., and R. W. Lanting. Atm. Environment. 6:943 (1972).

5. Van der Grinten, W. J. Ger. Offen. 2,237,793 (Feb. 22, 1973).

6. Reiszner, K. D., and P. W. West. Environ. Sci. & Technol. 7:526 (1973).

3.2.4.2 Nitrogen Dioxide

A. Principles Involved

The general and specific considerations given for SO_2 apply equally well to NO_2. Because of the greater reactivity of NO_2, apparently the only membrane materials that have sufficient oxidative stability are the perfluoro materials. Thus, materials like Teflon, FEP, or Kel-F are suggested for impregnation of the perforated stainless steel sheet. Conventional melt or solution processing is possible with FEP and Kel-F. For Teflon, *in situ* radiation-initiated polymerization of the monomer is required. A method for making pinhole-free composites of porous graphite, bronze, or silica with tetrafluoroethylene or chlorotrifluoroethylene has been patented recently (Ref. 1).

B. Physical Characteristics

The calibration output requirements for NO_2 are approximately those for SO_2, thus requiring a 0.001 to 0.003 cm^3/min flow rate of NO_2. This is a rate achievable with FEP and possibly with Kel-F, although the latter material has not been investigated as much.

The portable unit dimensions and weight would be the same as those for the SO_2 unit, since the only difference in the unit is the membrane material.

C. Operational Requirements

The same as those for the SO_2 unit.

D. Maintenance Requirements

The same as those for the SO_2 unit.

E. Shipping Requirements

The same as those for the SO_2 unit.

F. Estimated Accuracy

The same as that of the SO_2 unit - $\pm$ 2%.

F. Estimated Cost

Development costs would be higher than for the sulfur dioxide source because of the in situ polymerization technique used to form the membrane. Our estimate is $50,000. Other costs would be the same as for the SO_2 source.

2) Production - same as those for the SO_2 unit.

H. Advantages/Disadvantages

The same as those for the SO_2 unit except for possible NO_2 compositional changes with time and the possibility of more rapid deterioration of the membrane.

I. Design Sketch

The same as that for the SO_2 unit as shown.

J. Recommendation

Undertake development of the permeation device.

K. References

1. Roesinger, S., W. Ulsamer, and G. Pietzka. Ger. Offen. 2,108,363, Sept. 7, 1972.

3.2.4.3 Carbon Monoxide

A. Principles Involved

The same method needed for SO_2 is also applicable to CO. Polydimethyl siloxane is proposed as the membrane material. Because of its high permeability characteristics, a wide latitude in design and operating temperatures is possible.

B. Physical Characteristics

The calibration output requirements for CO are 10 times those of NO_2, thus requiring a 0.05 to 0.15 cm^3/min flow rate of CO. With the use of polydimethyl siloxane, this rate is still lower than that possible with the pure polymer.

The portable unit dimensions and weight would be the same as those for the SO_2 unit.

C. Operational Requirements

The same as those for the SO_2 unit.

D. Maintenance Requirements

The same as those for the SO_2 unit.

E. Shipping Requirements

The same as those for the SO_2 unit.

F. Estimated Accuracy

The same as that of the SO_2 unit - $\pm$ 2%.

G. Estimated Cost

1) Development - the same as that for the SO_2 unit.

2) Operation - the same as that for the SO_2 unit.

H. Advantages/Disadvantages

The same as those for the SO_2 unit.

I. Design Sketch

The same as that for the SO_2 unit.

J. Recommendation

Undertake development of the permeation device.

3.2.4.4 Ozone

Ozone at temperatures above liquid nitrogen temperature is not stable. Thus, at -78°C about 9% of ozone decomposes in two weeks and a permeation tube approach to preparation of known and constant concentrations of ozone is not possible.

3.2.4.5 Butene-1

A. Principles Involved

The same considerations advanced for SO_2 are also applicable to butene-1. Polydimethyl siloxane is proposed as the membrane material. However, this material may have flow rates much in excess of those required, and a silicone copolymer such as silicone-carbonate may be a better candidate.

B. Physical Characteristics

The calibration output requirements for butene-1 are the same as those for NO_2, thus, requiring a 0.005 to 0.015 cm^3/min flow rate of butene-1. This is several orders of magnitude lower rate than achievable with pure dimethyl siloxane.

The portable unit dimensions and weight are the same as those for the SO_2 unit.

C. Operational Requirements

The same as those for the SO_2 unit.

D. Maintenance Requirements

The same as those for the SO_2 unit.

E. Shipping Requirements

The same as those for the SO_2 unit.

F. Estimated Accuracy

The same as that of the SO_2 unit - $\pm$ 2%.

G. Estimated Cost

1) Development - the same as that for the SO_2 unit.
2) Operation - the same as that for the SO_2 unit.

H. Advantages/Disadvantages

The same as those for the SO_2 unit.

I. Design Sketch

The same as that for the SO_2 unit.

J. Recommendation

Undertake development of the permeation device.

3.3 Chemical Methods

The derivation of test atmospheres from chemical changes is competitive with physical techniques. The most prominent example of such a method is the photolysis of oxygen to ozone stimulated by ultraviolet radiation. In considering possible methods for chemical generation of test atmospheres, the following categories are apparent: radiation stimulated changes (e.g., photolysis and radiolysis), thermally stimulated decomposition, energetic reactions in plasmas, electrolytic decomposition, and reactions by mixing. In chemical reactions, when the only gaseous product is the desired pollutant gas, then, following the model employed for physical methods, the chemical species act as a storage media for the pollutant, and the reaction, when it is rate controlled, performs the function of a dispensing mechanism. When more than one gaseous product results from the reaction, then the effect of the other gases on instrument calibration must be considered. The presence of other gaseous reaction products may interfere with the attainment of suitable test atmospheres and thus negate the use of the method.

Generally, it is difficult to identify reaction processes controllable at the rates required in test atmosphere generation. Thus chemical methods tend toward greater complexity than do physical methods. A possible exception is the application of electrochemical decomposition, not to generate a pollutant but to control the rate of discharge of a pollutant from a storage volume.

3.3.1 Radiolysis, Photolysis, and Thermolysis

Both photolysis and radiolysis involve the breaking up or activation of molecular species by high energy radiation such that the subsequent recombinations result in the derivation of the desired pollutant species. The only difference between the two techniques is in the source of radiation; photolysis employs ultraviolet light quanta, while radiolysis employs emanations from nuclear reactions. Thermolysis achieves the same result but with lower energy consisting primarily of decomposition by

heating.

In general, thermolysis is more readily applied and provides less complexity than do radiolysis or photolysis. Particularly for high molecular weight compounds, the results of the high energy methods are complex mixtures of reactant products. For thermolysis, specific bonds are broken at fixed temperatures thereby providing well-defined decomposition products.

Chemical species can act as an efficient storage medium for a pollutant gas; however, usually the control of the dispensing of the gas is not possible in a decomposition reaction. Characteristically, the rate of reaction is a logarithmic function of temperature. Typically, the decomposition can be a simultaneous radical chain reaction as well as a molecular reaction. Thus, a batchwise injection of the generated gas in a mixing/dilution bag is indicated for most cases.

Many reactions that produce a selected contaminant also produce additional products or generate unwanted side reactions. These byproducts in certain cases may have to be removed which complicates the system. Finally, if a batch process is the only way to do it, because of the small amounts of dopant gases involved, very small amounts of the starting material (a few milligrams or less) are required, which may affect the precision of the measurements.

3.3.1.1 Sulfur Dioxide

A. Principles involved - The compound that we are proposing to use in a batchwise process, in the absence of the knowledge about its decomposition rate characteristics for a continuous process, is a coordinated iridium complex of the following structure (Ref. 1):

$$[(SO_2)_2\ Ir\ (\phi_2P\text{-}CH_2CH_2\text{-}P\phi_2)_2]Cl \qquad \phi = \text{phenyl}$$

This is only one member in a family of coordinated iridium complexes that form adducts with a very wide variety of gases including oxygen and hydrogen. It decomposes cleanly according to the reaction below:

$$[(SO_2)_2\ Ir\ (\phi_2P\text{-}CH_2CH_2\text{-}P\phi_2)_2]Cl \xrightarrow{238°C} [Ir(\phi_2P\text{-}CH_2CH_2\text{-}P\phi_2)_2]Cl + 2\ SO_2\uparrow$$

Furthermore, it is a compound with a high molecular weight (1152), is prepared easily in high yield (85-95%) (Refs. 1, 2), is stable in the solid state and does not require a too high temperature (238°C) for its complete decomposition. Once it has been decomposed to generate the pollutant, it can be regenerated with more SO_2 and used again.

B. Physical characteristics - The calibration output requirements for SO_2 have been specified as 0.005 ppm (13.1 ug/m^3) as the minimum limit with the field usable test atmosphere generating device delivering the doped air at 1 ℓ per minute (lowest rate) for periods up to 2 hr. Thus, the minimum volume (120 ℓ of doped air would require 0.0006 cm^3 (2.7×10^{-5} mmol) of SO_2. This small quantity of SO_2 could not be obtained directly in a precise manner. Thus, several dilution steps of conveniently doped air would have to be involved. For example, for the purposes of illustration the following steps could be taken: 1) decompose 15.552 mg of the iridium compound into 1.2 ℓ of zero air, which will result in a 5000 ppm SO_2 concentration; 2) dilute this in three successive 1 to 100 dilution steps to obtain the required 0.005 ppm (13.1 ug/m^3) SO_2 doped air. If a Cahn Electrobalance is used in weighing out the sample, one of the dilution steps could be eliminated by weighing out a proportionately smaller sample. Cahn Electrobalances are accurate to ± 0.001 of a milligram in a milligram range. The compound would be weighed out in a quartz tubing (0.6 cm diameter x 15.2 cm length) and positioned in the middle of the tubing and plugged with glass wool at both ends. For decomposition purposes the center part of the tubing would be fitted with a heating tape or a microfurnance.

At the instrument site, a supply or source for zero (clean) air is required. This may be either a compressed tank of clean air or an air scrubbing system. Alternatively, zero air source can be a part of the portable test atmosphere generating unit proposed.

The entire unit including compressed zero air lecture bottle, dopant source tube and mixing/dilution bag (up to 360 ℓ capacity) would have the following physical characteristics:

Total weight: 3.4 kg

- air lecture bottle, 2.3 kg
- dopant tube, valve, tubing, 0.2 kg
- mixing/dilution bag, 0.9 kg

Total unit dimensions: 45.7 x 30.5 x 7.6 cm.

- air lecture bottle, 38.1 x 5.1 cm diameter
- source tube, 0.6 x 15.2 cm
- mixing/dilution bag ~ 12.7 x 12.7 x 2.5 cm when collapsed; inflated ~ 88 cm diameter sphere for 360 ℓ volume.

C. Operational requirements - The operation of the unit consists of connecting the source tube by means of Teflon connectors to the clean air line; plugging in the heater, set to produce a predetermined temperature (240°C) inside the tube; and subsequently delivering the required amount of air through the source tube into the mixing/dilution bag. If several dilution steps are involved, additional metering in successive dilution bags would be involved.

D. Maintenance requirements - Little maintenance should be required other than regular flushing of the mixing bags after use.

E. Shipping requirements - None beyond the normal parcel post packaging. The source compound is air stable.

F. Estimated accuracy - The estimated accuracy in a batch operation will be determined by the accuracy of weighing out the solid sample and the accuracy of dilution steps. A sample on a Cahn Electrobalance can be easily weighed out ± 0.01% in the sample weight range required. Thus, the accuracy with which the dilution steps are conducted becomes the limiting factor; however, an accuracy of ± 10% should be achievable.

G. Estimated cost - Development costs to assemble, test, and calibrate this method are estimated to be $40,000. In operation, the generation of test atmospheres would be under $10 for materials.

H. Advantages/Disadvantages - This method is relatively straightforward and has a minimum of support requirements. Until found otherwise the approach may be capable of only a batchwise operation.

I. Design Sketch -

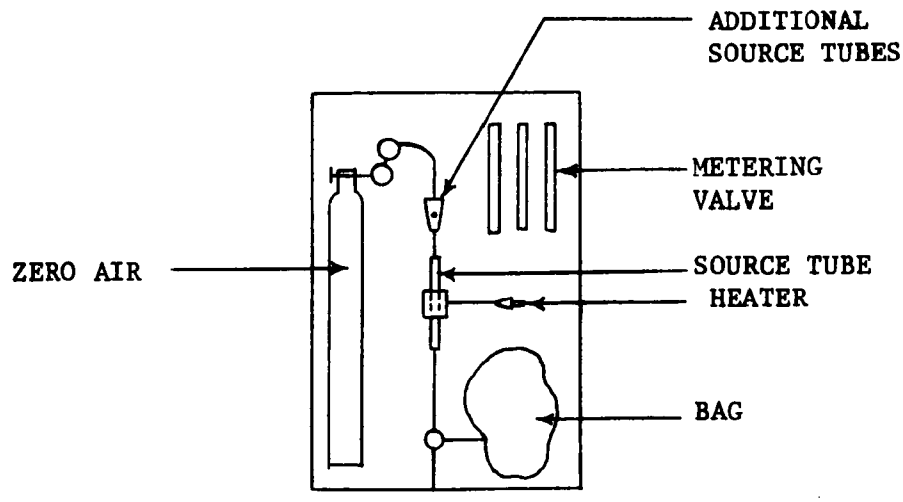


Figure 3-12. Thermolysis test atmosphere generator.

J. Recommendation - Investigate decomposition kinetics for possible development of continuous doping process.

K. References

1. Vaska, L., and D. L. Catone. J. Am Chem. Soc. 88:22, 5324 (1966).

2. Vaska, L., and J. W. DiLuzio. J. Am. Chem. Soc. 83:2784 (1964).

3.3.1.2 Nitrogen Dioxide

A. Principles involved - The same general and specific considerations advanced for SO_2 generation apply to NO_2 generation. The coordinated iridium complex for NO_2 has the following structure:

$$[(NO_2)_2\ Ir\ (\phi_2P\text{-}CH_2CH_2\text{-}P\phi_2)_2]Cl$$

The compound is prepared from $[Ir\ (\phi_2P\text{-}CH_2CH_2\text{-}P\phi_2)_2]Cl$ and NO in air which leads to the nitrogen dioxide adduct. The compound decomposes according to the following reaction:

$$[(NO_2)_2\ Ir\ (\phi_2P\text{-}CH_2CH_2\text{-}P\phi_2)_2]Cl \xrightarrow{163°C} [Ir\ (\phi_2P\text{-}CH_2CH_2\text{-}P\phi_2)_2]Cl + 2NO_2\uparrow$$

B. Physical characteristics - The calibration output requirements for NO_2 have been specified as 0.01 ppm 18.8 ug/m^3 at the lower limit with the

field usable test atmosphere generating device delivering the doped air at 1 ℓ/min (lowest rate) for periods up to 2 hr. Thus, the minimum volume (120 ℓ) of doped air would require 0.0012 cm^3 (5.4×10^{-5} mmol) of NO_2. The same dilution approach would have to be used for NO_2 as for SO_2. The amount of the iridium compound required to give 10,000 ppm NO_2 in 1.2 ℓ of zero air is 30.132 mg. This amount could be decreased so as to eliminate one of the dilution steps. The weight and dimensional considerations are the same as for the SO_2 unit. Because of the greater reactivity of NO_2, stainless steel and Teflon are the preferred materials for handling it. The mixing/dilution bags, for example, would have to be made of FEP Teflon. As a general rule systems handling NO_2 require prior conditioning with the gas.

C. Operational requirements - The same operational requirements as for the SO_2 unit apply except that the decomposition temperature of the iridium compound is lower (163°C).

D. Maintenance requirements - The same as those for the SO_2 unit.

E. Shipping requirements - The same as those for the SO_2 unit.

F. Estimated accuracy - The same considerations as those for the SO_2 unit apply--± 10%.

G. Estimated cost - 1) Development - the same as that of the SO_2 unit. 2) Operation - the same as that of the SO_2 unit.

H. Advangages/Disadvantages - The same as those for the SO_2 unit.

I. Design sketch - The same as that for the SO_2 unit.

J. Recommendation - Investigate decomposition kinetics for possible development of continuous doping process.

3.3.1.3 Carbon Monoxide

A. Principles involved - The same general and specific considerations advanced for SO_2 generation apply also for CO generation. The coordinated iridium complex for CO has the following structure:

$$[(CO)\ Ir\ (\phi_2P\text{-}CH_2CH_2\text{-}P\phi_2)_2]\ Cl$$

The compound decomposes according to the following reaction:

$$[(CO)\ Ir\ (\phi_2P\text{-}CH_2CH_2\text{-}P\phi_2)2]Cl \xrightarrow{260°C} [Ir\ (\phi_2P\text{-}CH_2CH_2\text{-}P\phi_2)_2]Cl + CO\uparrow$$

B. Physical characteristics - The calibration output requirements for CO have been specified as 0.5 ppm (572 ug/m^3) as the minimum limit with the field usable test atmosphere generating device delivering the doped air at 1 ℓ/min (lowest rate) for periods up to 2 hr. Thus, the minimum volume (120 ℓ) of doped air would require 0.06 cm^3 (2.7×10^{-3} mmol) of CO. Because of the large minimum requirement and the one-to-one molar relationship between the iridium complex and evolved CO, a one-step dilution from 120 mℓ to 120 ℓ would be sufficient. The amount of the iridium compound required to give 500 ppm (572.5 mg/m^3) of CO in 120 ml of zero air is 2.840 mg. The weight and dimensions are the same as for the SO_2 unit.

C. Operational requirements - The operation requirements are the same as for the SO_2 unit.

D. Maintenance requirements - The same as those for the SO_2 unit.

E. Shipping requirements - The same as those for the SO_2 unit.

F. Estimated accuracy - Because only one dilution step is involved, the accuracy could be as high as ± 5%.

G. Estimated cost - The same as that of SO_2 unit.

H. Advantages/Disadvantages - The same as those for the SO_2 unit

I. Design sketch - The same as that for the SO_2 unit.

J. Recommendation - Investigate decomposition kinetics for possible development of continuous doping process.

3.3.1.4 Ozone

A. Principles involved - The production of ozone must be done dynamically if continuous, constant, and reproducible mixtures with a diluent gas are to be achieved. This is due primarily to ozone's extraordinary reactivity and its decomposition to oxygen upon standing. Ozone is produced by ultraviolet illumination, electric discharge, and electrolytic techniques, and it may be obtained commercially in a semipurified state. Probably the most preferred method of laboratory ozone production is the use of ultraviolet irradiation.

According to Hodgeson, Stevens, and Martin (Ref. 1) the most promising approach to ozone generation is the ultraviolet photolysis configuration as practiced by Regener (Ref. 2) and Tommerdahl (Ref. 3). In their designs, an extremely stable, low-pressure mercury arc lamp irradiated a quartz tube through which the airstream flowed. A shutter or variable aperture between the lamp and quartz tube was used to vary the ozone output. By changing geometry, diluent flow rate, and aperture size, different ozone mass flow requirements can be met.

B. Physical characteristics - An example of the ozone source unit is that of Hodgeson, Stevens, and Martin (Ref. 1) and is depicted in Figure 3-13. The photolysis source is a low pressure mercury arc lamp. The lamp current is regulated at 18 mA with a constant current power supply and a constant voltage transformer. The quartz tubing is type T-20 Suprasil and has high transparency at 185 nm. The box containing lamp and tube is an enclosed system of 0.6 cm aluminum plate. A hollow aluminum tube fits around the lamp envelope and can be adjusted continuously to provide from zero to 100% shielding of the radiation incident on the tube.

The maximum output of an ozone source of the configuration shown in Figure 3-14 depends upon: 1) lamp size, 2) tubing, 3) inner surface reflectivity, 4) airflow rate, and 5) applied lamp voltage. By using an 8-inch lamp and 25 mm o.d.tubing, the maximum concentration of 2.1 ppm (4116 ug/m^3) of ozone at 10 ℓ/min. airflow rate can be obtained. To vary the concentration of ozone produced, it was found best to keep the airflow constant at the desired rate and vary the shielding of the lamp envelope. Thus, the generation of 0.005 to 1.0 ppm (9.8 to 1960 ug/m^3) ozone doped air at 1 to 3 ℓ/min flow rate presents no problems.

At the instrument site, a supply or source for zero (clean) air is required. This may be either a compressed tank of clean air or an air scrubbing system. The dimensions of the ozone source are 35.6 x 10.2 x 10.2 cm and the entire unit would require also a diaphragm pump, drying columns, needle valves, flowmeters, and the associated plumbing.

C. Operational requirements - The operation of the unit requires a clean air supply and normal electric power. The operation would consist

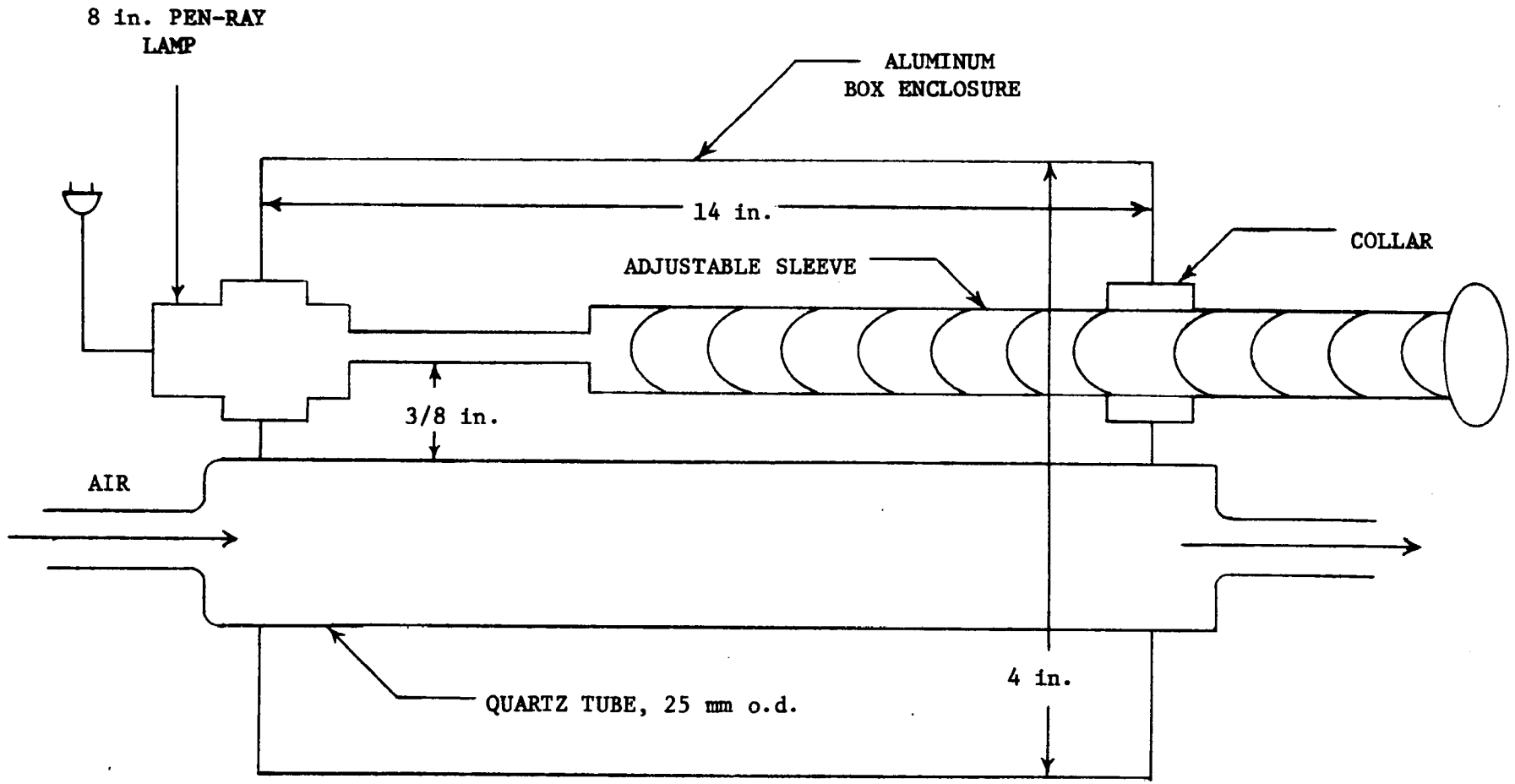


Figure 3-13. Ozone source.

of starting the diaphragm pump, adjusting for the desired airflow rate, plugging in the electrical supply for the generator and adjusting the shielding of the lamp envelope for the generation of the desired ozone concentration. Stabilization of the instrument is usually achieved within 10 minutes.

D. Maintenance requirements - The unit maintenance would consist primarily of periodic calibration of the instrument since the output of the source decreases with time. Short-term stability of the unit is excellent once provisions for constant airflow rate and elimination of fluctuations in line voltage are made.

E. Shipping requirements - Should the shipment of the ozone source, the diaphragm pump, and the associated plumbing be desirable, a box of the approximate dimensions of 0.6 × 0.3 × 0.3 m would be required.

F. Estimated accuracy - The accuracy of the described instrument is in the area of ± 3% for the high concentrations and ± 3-5% for the low concentrations.

G. Estimated cost - The cost of the instrument depends upon the design features one wants but would be expected to be in the general area of $500. The cost of operating the instrument would be minor. Development would cost approximately $25,000.

H. Advantages/Disadvantages - The ultraviolet ozone generator provides a dynamic test atmosphere generator that is reliable and simple to operate. It is, however, bulky and needs periodic recalibration. The cost may forbid wide use for the atmosphere generation.

I. Design sketch

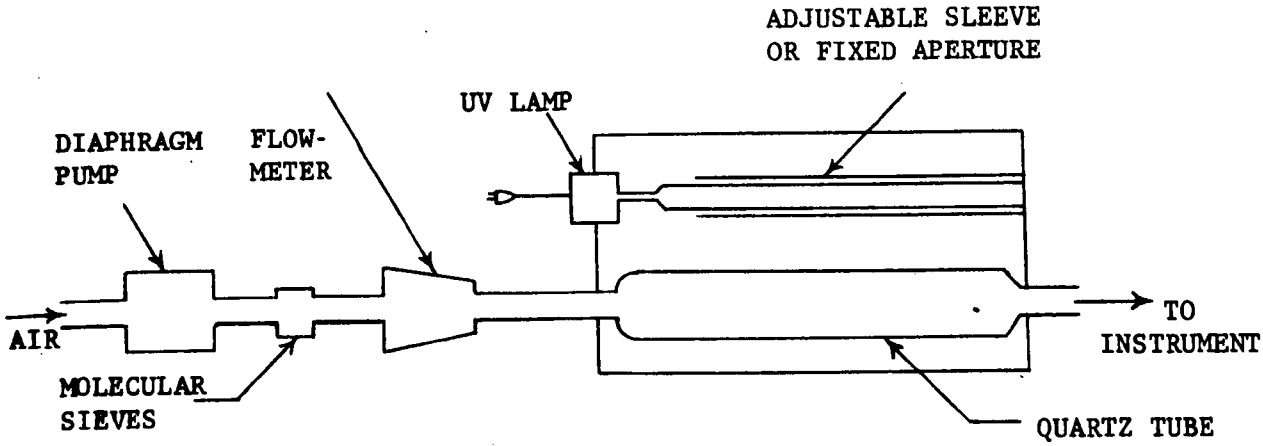


Figure 3-14. Ozone test atmosphere generator.

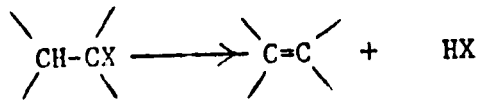
J. Recommendation - For ozone, the ultraviolet generator appears to be the best choice at this time.

K. References

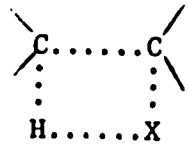
1. J. A. Hodgeson, R. K. Stevens, B. E. Martin, A paper on "A Stable Ozone Source Applicable as a Secondary Standard for Calibration of Atmospheric Monitors" presented at the Analysis Instrumentation Symposium, Instrument Society of America, Houston, Texas, April 1971.
2. Regener, V. H., J. Geophys. Res. 69:3795 (1964).
3. Tommerdahl, J. B. (Research Triangle Institute, Research Triangle Park, N. C.), Air Pollution Control Office, Environmental Protection Agency, Final Report--Part I, Contract No. CPA-22-69-7 (1969).

3.3.1.5 Butene-1

A. Principles involved - Gas-phase reactions that have been studied in some detail are of the following type:



where X = halogen. Many of these reactions are known as the four-center reactions because presumably, the transition state involves a structure in which four adjacent atoms are sharing their valence electrons:



Thus, if n-iodobutane is used in the pyrolysis reaction, the expected product would be butene-1

$$CH_3-CH_2-CH_2-CH_2-I \longrightarrow CH_3-CH_2-CH = CH_2 \uparrow + HI$$

B. Physical characteristics - The calibration output requirements for butene-1 have been specified as 0.05 to 5.0 ppm with the field usable test atmosphere generating device delivering the doped air at 1 to 3 ℓ/min for periods up to 2 hr. Since the concentration of the dopant gas required is low, either the turbulence of the diluent gas (nitrogen, air, etc.) can cause the required vaporization of the liquid or, alternatively, it can be atomized into an aerosol in the atomizer shown in Figure 3-15.

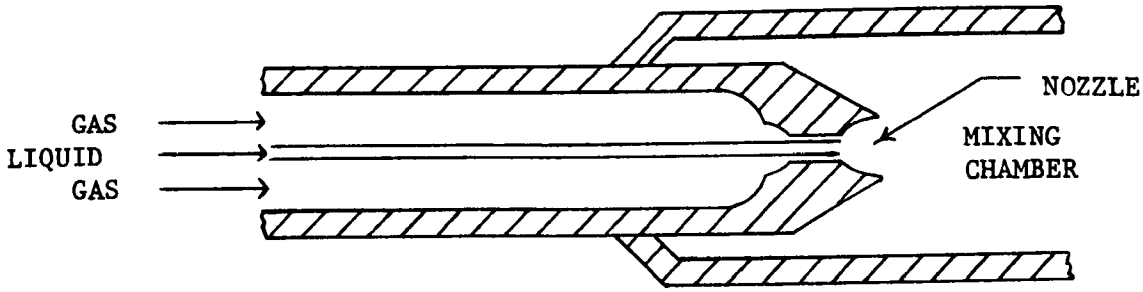


Figure 3-15. Aerosol generator.

Furthermore, many atomizer systems are available commercially which will produce known concentrations of gas or vapors for calibration work in the 1 to 2,000 ppm range. Such systems are accurate to ± 1% if a precision flowmeter is used for the diluent gas. After the liquid has been atomized, the mixed gas enters a quartz tube containing a ceramic core heater where the pyrolysis takes place, Figure 3-16.,

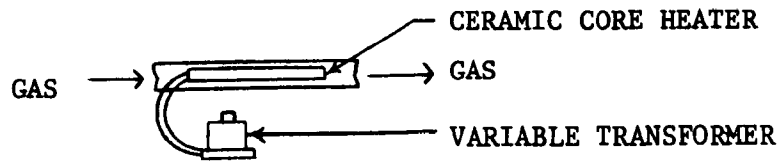


Figure 3-16. Pyrolysis gas generator.

and from there through a soda lime trap into the instrument. The kinetics of HI el mination, the pyrolysis temperature, and the iodobutane vaporization technique all need to be worked out.

At the instrument site, a supply or source for zero (clean) air or nitrogen is required. This may be either a compressed tank of clean air or an air scrubbing system. Alternatively, zero air source can be a part of the portable test atmosphere generating unit proposed.

The entire unit including compressed zero air lecture bottle, dopant source tube, and mixing/dilution bag (up to 360 ℓ capacity) would have the following physical characteristics:

total weight: 4.3 kg

-- air lecture bottle 2.3 kg
- atomizer, iodobutane 0.2 kg
- Pyrolyzing tube 0.5 kg
- soda lime scrubber 0.5 kg
- storage bag 0.9 kg

total unit dimensions: 45.7 x 30.5 x 10.2 cm

- air lecture bottle 38.1 x 5.1 cm diameter
- atomizer 7.6 x 2.5 cm diameter
- pyrolyzing tube 25.4 x 2.5 cm diameter
- soda lime scrubber 5.1 x 2.5 cm diameter
- storage bag ~ 12.7 x 12.7 x 2.5 cm when collapsed.

C. Operational requirements - The operation of the unit would require iodobutane, clean air supply, and normal electric power. The operation would consist of plugging in of the electrical supply for the pyrolyzing unit and adjusting for the desired air and iodobutane flow rates.

D. Maintenance requirements - The pyrolyzing tube and soda lime scrubber would require periodic replacement.

E. Shipping requirements - None beyond the normal parcel post packaging. Iodobutane is a high boiling liquid that would require a glass container.

F. Estimated accuracy - No kinetic pyrolysis data are available. Flow rate adjustments are capable of better than ± 10% so that an estimate accuracy of ± 10% is reasonable. However, experimental confirmation is required.

G. Estimated cost - A development effort is required that would.

cost on the order of $50,000 to assess the appliciability of this method. In operation, costs would be about $500 for each generator.

H. Advantages/Disadvantages - This could be the basis of a dynamic test atmosphere generator that is simple to operate. However developmental work is required.

I. Design sketch

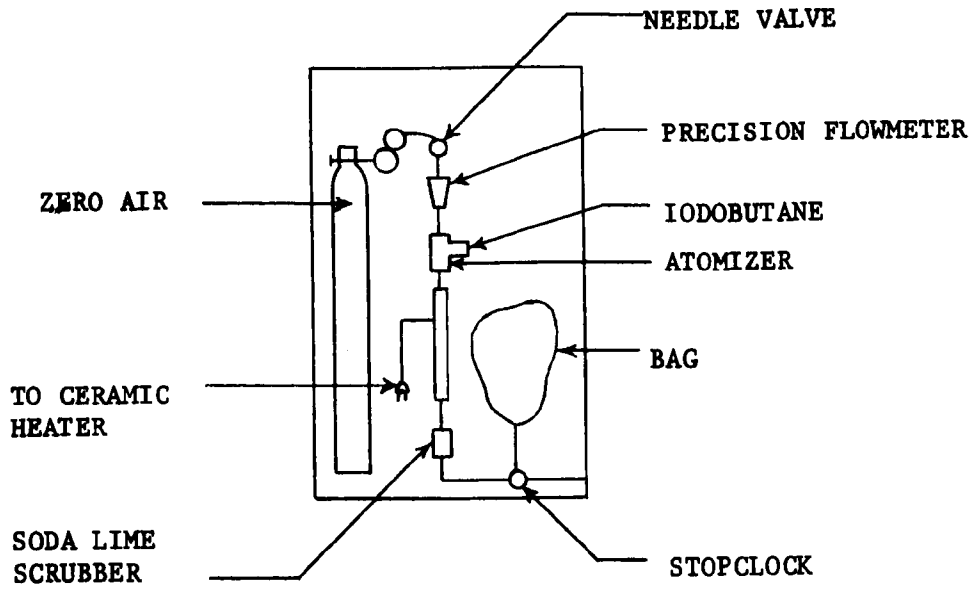


Figure 3-17. Pyrolysis test atmosphere generator.

J. Recommendation - Investigate decomposition kinetics for possible development of continuous doping process.

3.3.2 Plasma Discharge

A plasma is a gas consisting largely of charged particles. Plasmas may be produced by energetic particles or by quanta with sufficient energy to ionize and excite neutral gas molecules and atoms. Plasma physics concentrates on very high temperature systems but plasma chemistry is more concerned with low temperature plasmas such as are produced in discharge tubes. These are of interest because of the unique chemical reactions found in the presence of free neutral atoms, ions, and free radicals. Up until the last two decades, most plasma chemistry studies employed DC or low frequency electrode or electrodeless discharges. Now the RF and microwave discharge are predominately used to produce plasmas.

3.3.2.1 Sulfur Dioxide

A. Principles involved - Although no studies have been made of sulfur atoms produced in a discharge, there has been extensive study of reactions in oxygen plasmas. These have included the oxidation of elemental sulfur and investigation of SO, SO_2, and SO_3 reactions. The only apparent application of plasma generation to the preparation of SO_2 test atmospheres is through the oxidation of elemental sulfur or the reaction of sulfur compounds with atomic oxygen to produce SO_2. One such method is suggested here.

A strip of filter paper impregnated with a predetermined amount of the sulfur or a sulfide (polysulfide) serves as the storage medium for the pollutant. In order to generate the test atmosphere, the filter paper is subjected to a plasma discharge in clean air such that all of the sulfide is oxidized thereby producing a known quantity of sulfur dioxide. This is diluted by mixing with zero air and employed as a test atmosphere. The preparation and distribution of sulfur sources require a minimum of effort and equipment. The filter paper impregnation technique, although not tested, should be easy. It requires that between 1 and 500 µg of releasable sulfur be available for the required dilution.

At the instrument site, a supply or source for zero (clean) air is required. This may be either a compressed tank of clean air or an air

scrubbing system. Since these are common to a number of generation concepts, they are discussed elsewhere.

The plasma source will consist of a small RF generator which drives a coil. The coil surrounds a glass tube in which is placed the calibrated sulfur source. The tube is flushed with zero air and its pressure reduced to below 10 torr by means of a diaphragm pump. The tube is closed off and the RF generator turned on. A discharge is maintained in the tube for 10 minutes. This creates active oxygen atoms which react rapidly with the sulfur containing source to produce sulfur dioxide. After completing the oxidation, the plasma tube is filled with zero air and the mixture, further diluted with air, is stored in a plastic bag. This constitutes the test atmosphere.

For a 360 liter bag, the source must contain 516 μg of sulfur for a 1 ppm (2617 $\mu g/m^3$) concentration level. Other pollutant concentrations are readily calculable from this number. It may be more efficient to vary the concentration by providing different lengths of filter paper with a standard sulfur content per unit length.

B. Physical characteristics - The sulfur source is a strip of impregnated filter paper weighing about 20 g, and a test atmosphere generator is required at field site consisting of the following components:

1. Zero air supply - Available in cylinders containing over 6000 ℓ.
2. RF generator - Electronic cabinet with approximate dimensions of a cube with 0.5 m edges requiring 115 VAC supply at 100 W and with a mass of about 9 kg.
3. Plasma tube, plumbing and holding bag - The collapsible holding bag will have a volume of 360 ℓ (if spherical, a radius of 44 cm). The plasma tube and plumbing will have a small volume and mass. A standard wet test meter is required to measure the total volume of dilutant air.

C. Operational requirements - Source preparation consists of processing of a quantity of impregnated filter paper, testing the batch for sulfur content and uniformity, and storage in a passive environment until used. For test gas generation, the sulfur impregnated paper is oxidized to SO_2 in a plasma and used to prepare a dilute test atmosphere. Apparatus

and supplies include

1. Clean air source (360 ℓ @ STP),
2. An RF generator,
3. 115 VAC supply,
4. A wet-test meter or rotameter,
5. Tubing, valves, and plasma tube, and
6. A plastic bag.

D. Maintenance requirements -

1. RF generator - No maintenace other than that occasioned by reduced output or failure.
2. Plumbing, plasma tube, and bag - Flush after use and hold for reuse. Check integrity on reassembly.
3. Wet test meter or rotameter - Normal use requires little or no maintenance.

E. Shipping requirements - These are minimal consisting of one large brown envelope.

F. Estimated accuracy - Estimate ± 10% (requires experimental confirmation)

G. Estimated costs - Development costs are estimated to be approximately $50,000. Source cost depends on volume of use. The total cost of 100 samples will be approximately the same as for 1000 samples. Setup and testing costs are major items as follows:

Initial setup	$2,000
Cost per run	$2,000

Assuming 1000 samples per run, the cost, including handling and distribution, is approximately $5 per test. The apparatus required at the test site is as follows:

RF generator	$500
Plasma tube	200
Wet test meter	500
Plumbing and bag	100
Zero air in cylinder with regulator	150
Total cost	$1450

H. Advantages/Disadvantages - The method has as its strongest point the simple sample preparation and distribution. However, it requires an RF source at each test site and is subject to possible interferences from other active plasma species.

I. Design sketch - See Figure 3-18.

J. Recommendations - This technique merits consideration but since it hasn't been used or tested, experimental confirmation is required. Consideration should be given to possibilities for use of station apparatus for other types of test atmospheres.

K. References

1. Halstead, C. J., and B. A. Thrush. Nature. 204:988 (1964).
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4. McTaggart, F. K. Plasma Chemistry in Electrical Discharge. N.Y., Elsevier Publishing Co., 1967.

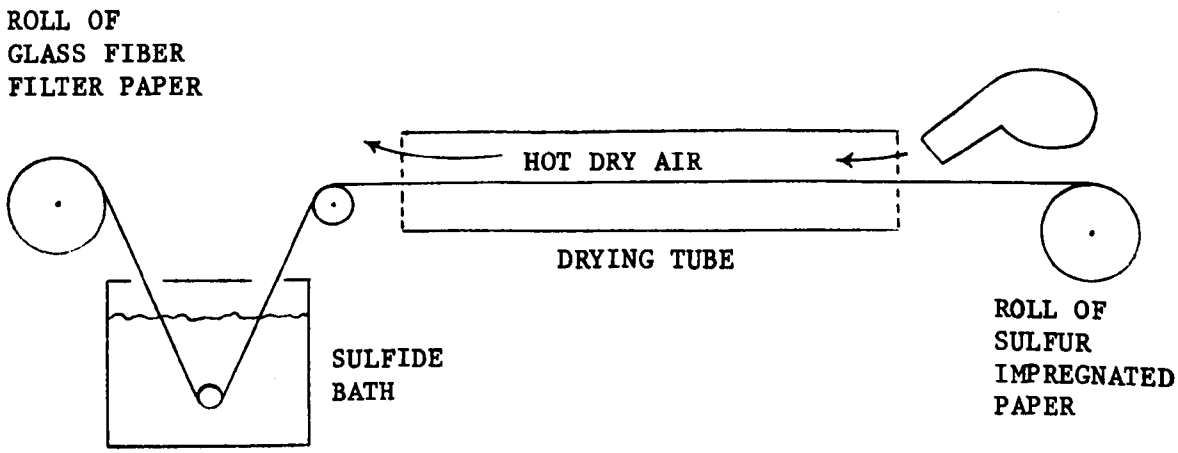
3.3.2.2 Nitrogen Dioxide

A. Principles involved - Production of NO_2 directly in a plasma discharge is complicated by the various reactions producing NO, N_2O_5, N_2O, and active nitrogen and oxygen. These various species are found to exist in various proportions with no well-defined stability criteria. However, if a controlled amount of NO is generated quantitatively by another method and is mixed with an excess of plasma-produced ozone in a reaction chamber, then NO_2 can be generated quantitatively.

Nitric oxide is produced quantitatively in an electrolytic cell containing nitrosyl hydrogen sulfate in concentrated sulfuric acid as illustrated in Figure 3-19. The NO is generated at the platinum cathode while oxygen is generated at the anode. In the electrolyte, the reaction is

$$NO^+ + e^- \rightarrow NO$$

Since only one electron is required per NO molecule, the rate of NO



SAMPLE PREPARATION

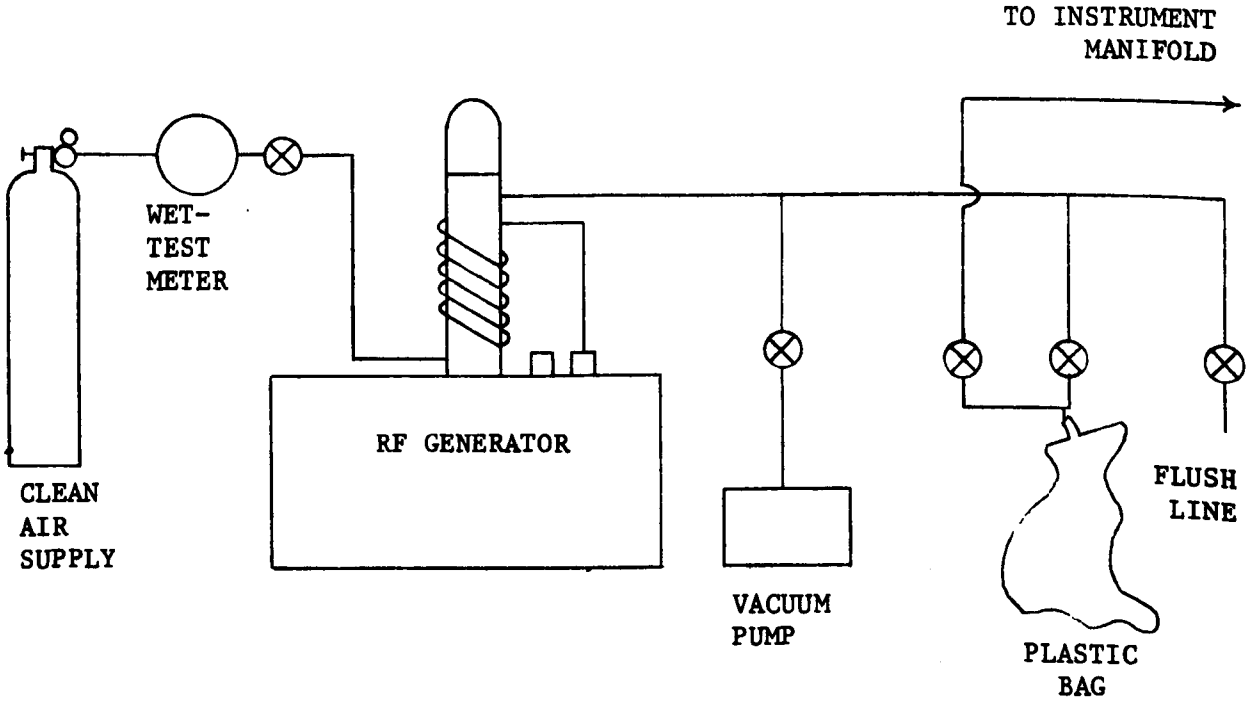


Figure 3-18. Plasma test atmosphere generator.

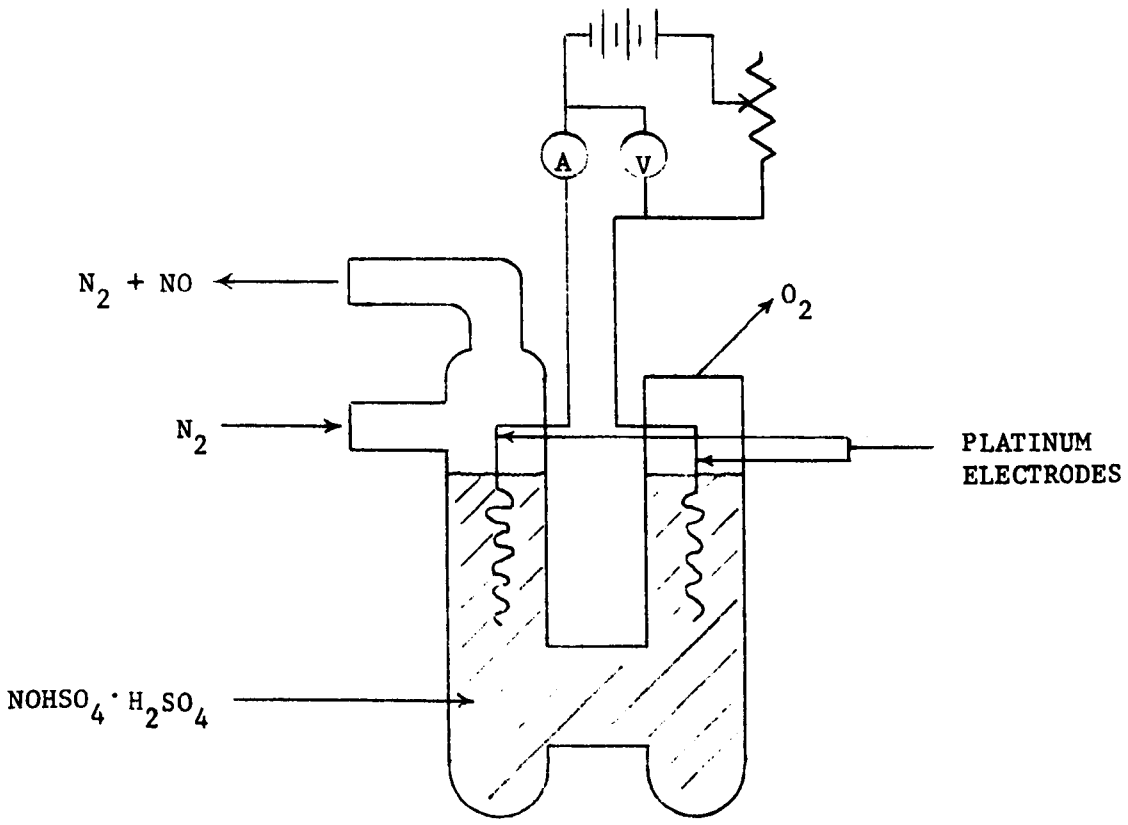


Figure 3-19. Electrolytic cell for quantitative NO generation.

generation is given by

$$q_E = I/zF$$

where

q_E = rate of gas generation, mole s^{-1}

I = electric current, A

z = number of electrons required for each generated gas (z = 1)

F = Faraday's constant (9.65×10^4 C mol^{-1})

Since this is also the rate determining reaction for NO_2 production, and a concentration of NO_2 in the range 0.05 to 5 ppm (9.4 to 9400 $\mu g/m^3$) is required at flow rates from 1 to 3 ℓ/min, one may calculate the cell current required. This is in the range from 3.59 to 1.08 mA, the former current corresponding to a concentration of 0.05 ppm (94 $\mu g/m^3$), and a flow rate of 1 ℓ/min and the latter to 5 ppm and 3.4 min.

The generated NO would be mixed with ozone, produced in a silent discharge, in a reaction chamber and passed over hot glass beads to remove excess ozone and to decompose the small amounts of N_2O_5 produced. Nitrogen pentoxide results when the excess of ozone reacts with NO_2 by the reaction

$$2NO_2 + O_3 \rightarrow N_2O_5 + O_2$$

while the thermal decomposition reaction is

$$2N_2O_5 \rightarrow 4NO_2 + O_2$$

This ozonization of NO produces a dynamic test atmosphere for NO_2 measuring instruments. The critical control parameters are the cell current and the test atmosphere flow rate.

B. Physical characteristics - Because of the nature of this test atmosphere generation system, a "suitcase" design is described. In this O_2, N_2, zero air, and electric power connnections are made to a generation unit, the unit is turned on, and in ten minutes it is generating the test atmosphere with a continuous flow. It will continue to generate for 200 hours for each gram of dissolved $NOHSO_4$. Since the NO_2 generation rate is precisely controlled within the instrumentation, only the total flow of the test atmosphere requires measurement.

Referring to Figure 3-20, the "suitcase" contains:

a. an electrolytic cell with a preset constant current power supply,

b. an ozone generator consisting of a discharge tube and a stabilized high voltage source,

c. a reaction tube,

d. a glass-bead loaded heated column with an automatic temperature controller, and

e. associated flow lines and a mixing chamber.

Since only 0.01 g of the solute, $NOHSO_4$, will be required for a 2 hour run at a maximum concentration level, the electrolytic cell will require infrequent recharging. The N_2-O_2-NO_2 doping gas flow rate of about 100 ml/min will necessitate a 10-minute period to reach the equilibrium level if the column and reaction cell have volumes of about 250 cc.

C. Operational requirements - Cylinders of nitrogen and oxygen are required. A lecture bottle of prepurified nitrogen or oxygen contains 56 ℓ which is sufficient for 18 hr of test atmosphere generation. (Cost ∿ $26, gross wt. - 33 kg, size 20.3 x 68.5 cm, 2 stage regulator with flowmeter cost ≈ $150.

Zero air is also required. A No. 2 cylinder of zero air contains 2400 ℓ which is sufficient for six hours of operation at the maximum rate (Cost ∿ $26, gross weight ∿ (33 kg), size 20.3 x 68.5 cm, 2-stage regulator with flowmeter cost ∿ $150.

A 117 VAC power source is required.

D. Maintenance requirements - The electrolytic cell must be cleaned and the electrolyte replaced after every 100 hours of operation and must be constructed so as to be spill-proof. Otherwise no routine maintenance is required.

E. Shipping requirements - If all gases are to be carried with the unit, it is estimated that the total weight will be close to 63.6 kg. If gases are available at the site, the unit should weigh about 18.2 kg. The electrolytic cell and gas cylinders must be separately packed for shipment.

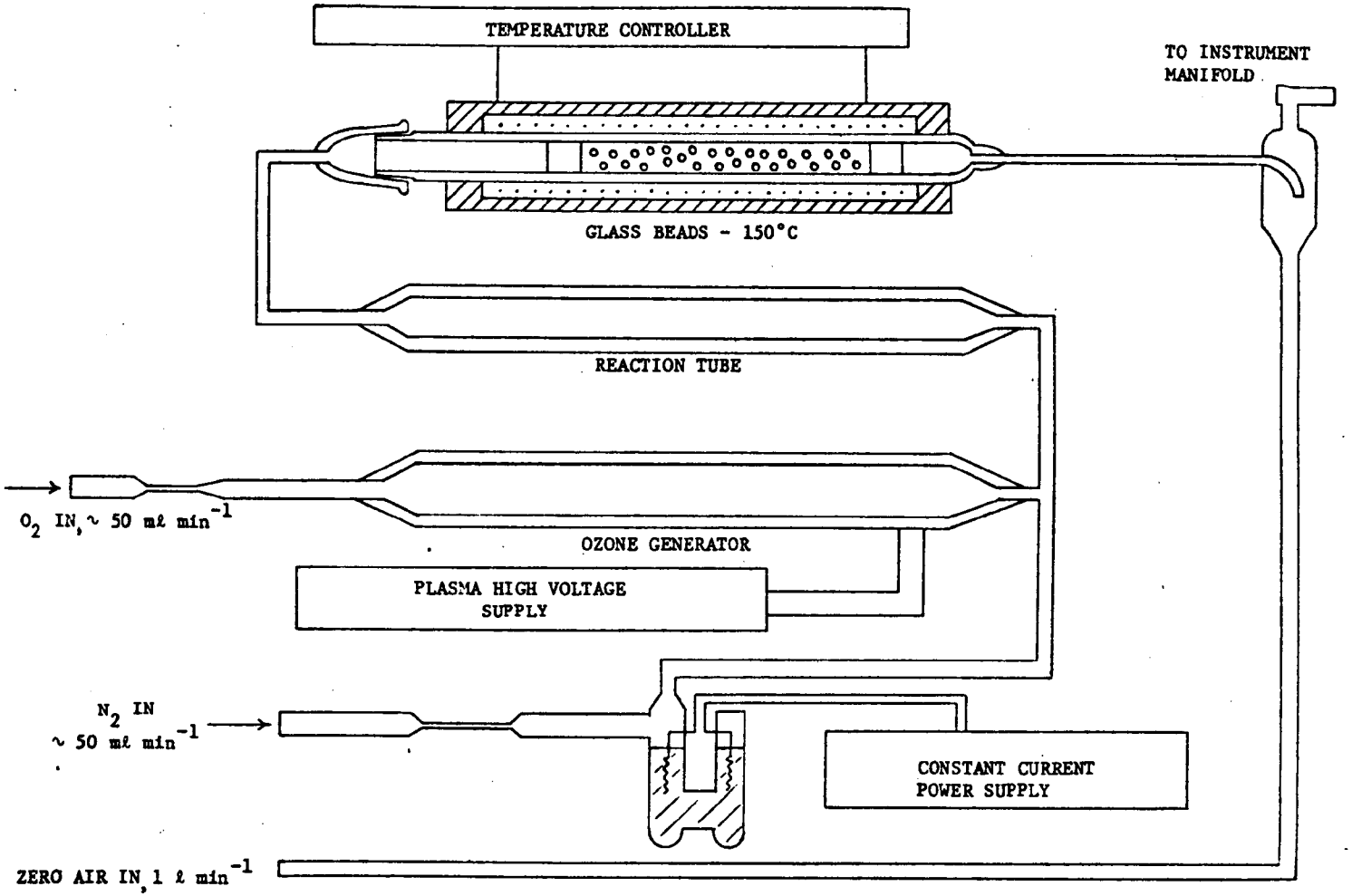


Figure 3-20. Nitrogen dioxide test atmosphere generator.

F. Estimated accuracy - Capable of < 10% error but will realistically provide 20% with untrained personnel.

G. Estimated costs - Development cost are estimated to be approximately $50,000. The costs of a complete generation set-up are as follows:

Gases and regulators, valves, and flowmeters	$375
Ozone generator	500
NO generator and power supply	200
Plumbing and glass bead column	200
Oven and controls	300
Cabinet case	300
	$1875

This cost is for one unit capable of frequent repetitive use.

H. Advantages/Disadvantages

Advantages
1. Self contained
2. Continuous flow

Disadvantages
1. Weight and cost
2. Untested

I. Design sketch - See Figure 3-20.

J. Recommendations - Consider trade offs between a complex generator like this and a predoped gas mixture with mixing and flow controls.

K. References

1. T. Singh, R. F. Sawyer, E. S. Starkman, and L. S. Caretto, Rapid Continuous Determation of Nitric Oxide Concentration in Exhaust Gases", J. Air Pollution Control Assoc., 18, 102, Feb. 1968.
2. G. O. Nelson, Controlled Test Atmospheres, Ann Arbor Science Publishers, Inc., Ann Arbor, Mich. 1971.
3. J. T. Shaw, "The Measurement of Nitrogen Dioxide in the Air", Atmos. Enviro., Pergamon Press 1 81-85, 1967.

3.3.2.3 Carbon Monoxide

Although there is some evidence that acetylene reacts in an oxygen

plasma to produce carbon monoxide, the further oxidation of this to carbon dioxide has also been observed. This prohibits the use of this reaction for obtaining test atmospheres of carbon monoxides. It may be possible, however, to find an organic compound which reacts in a plasma to produce carbon monoxide. Preferably this would be accomplished by impregnating filter paper with a known quantity of the organic compound and activating it in the plasma of an inert gas.

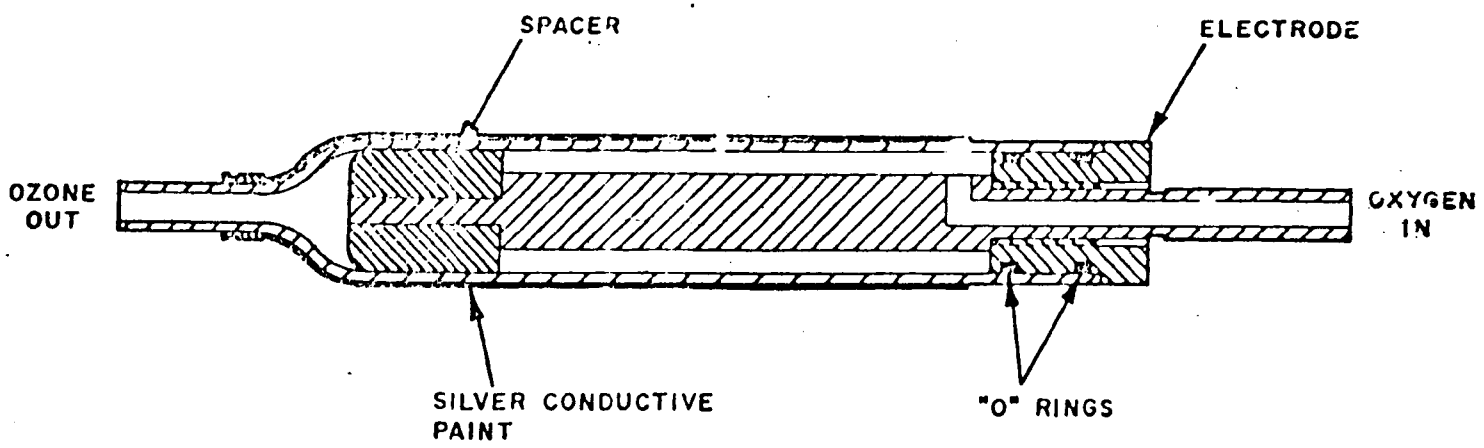
An alternative suggestion is to expose filter paper with a known releasable carbon content to a carbon dioxide plasma such as to reduce a known amount of the CO_2 to CO. Although there is no experimental evidence that this would be successful, it appears promising. It would require the same procedures and equipment as employed for SO_2 plasma generation except for the addition of a source of pure CO_2 with which to fill the plasma tube. Costs, if successful, would be of the same magnitude as those for SO_2 atmospheres.

3.3.2.4 Ozone

A. Principles involved - Most of the ozone required for industrial applications is generated by means of plasma discharges. For these purposes a large variety of ozonizers have been designed and some of them are commercially available. These units have efficiencies as high as 3.8×10^{-5} $g^{J^{-1}}$ (approximately 140 g of ozone per kw-hr of energy) when pure oxygen is employed--less when air is used. Where generation efficiency is required, dry air and low operating temperatures are employed.

An ozone test atmospheric generating device based upon plasma discharge can be provided. An ozonizer tube similar to the type that would be used in such a generator is shown in Figure 3-21. When an oxygen containing gas is allowed to flow through such a tube and a high voltage, (approximately 16kV) is applied between the inner and outer electrodes, a discharge takes place and ozone is generated.

Low flow rate ozonizers of this type are not usually employed for applications requiring a calibrated source. Stabilization and calibration



Note: Approximately 15 kv is applied between the silver conductive paint and the electrode in the form of pulses at a 16 Hz rate.

Figure 3-21. Instrument ozonizer.

are therefore a prime problem to be encountered in providing a plasma generator as a source for test atmospheres. There is no identificable reason however why such a source cannot be obtained.

The principle to be employed in test atmosphere generation of ozone is that employing an ozonizer tube as described above. The generation rate will be controlled by two parameters; the oxygen content of the gas in the discharge and the power supplied to the discharge. With respect to the first of these, an oxygen-inert gas mixture will be employed in order to avoid complex reactions which are possible for more active constituents in a plasma. Since high voltage is commonly supplied to the discharge tube in the form of pulses from an ignition coil, the most obvious method for controlling the energy input is to control the frequency with which pulses are supplied. This can readily be accomplished with a minimum of complex circuitry. For a given plasma energy and partial pressure of oxygen, the efficiency of ozone generation will depend on the reaction cross section between the atomic oxygen produced in the discharge and oxygen molecules. Testing is necessary to determine this efficiency for the various plasma conditions and to determine the efficacy of the approach.

Alternative techniques for quantitative generation of ozone in a plasma could involve; 1) the use of pressures lower than atmospheric in order to stabilize the plasma, 2) the use of chemical sources to supply oxygen to the plasma in order to provide quantitative control, or 3) the use of a pure oxygen supply with additional dilution.

B. Physical characteristics - The general principle for providing a calibrated plasma source for ozone test atmospheres is described in the preceding section. Ozone will be extracted from an oxygen-inert gas plasma. In a 500 cm^3 plasma tube operating at atmospheric pressure with the oxygen partial pressure at 1 torr (1.3×10^2 Nm^{-2}) and assuming 100% conversion (2 ozone molecules produced for each 3 oxygen molecules supplied), then the ozone produced would give a concentration of 1.2 ppm (2352 $\mu g/m^3$) in a 360 ℓ test atmosphere. If the conversion efficiency is 8%, then the concentration would be about 0.10 ppm (196 $\mu g/m^3$). Low concentrations are

obtainable by reducing the oxygen partial pressure, by changing the dilution, or by changing the plasma energy. While these numbers apply to a static atmosphere generator, they equally apply to a dynamic system which provides continuous generation. Also it is important to note that the numbers given are representative but do not represent the actual efficiencies which will be obtained in a calibrated ozonizer with variable energy input. These numbers would be obtained through testing.

The ozone test atmosphere generator will consist of an ozonizer tube and its associated supply plus the plumbing and accessories necessary to control gas flow rates and provide dilution. A diagram for a proposed system is shown in Figure 3-22. Air will be supplied to the mixing chamber through a rotometer and valve. It can be atmospheric air supplied through a pump with filtering and scrubbing of air from a compressed storage container. The ozonizer requires a supply of an inert gas-oxygen mixture at a controlled low flow rate, approximately 100 ml/min. At this rate, a lecture bottle containing the gas mixture would last for over 6 hr.

C. Operation requirements - Samples on which to base the ozone content of the test atmospheres are distributed in the form of lecture bottles containing inert gas-oxygen mixtures in various controlled proportions. The generator in addition requires a supply of clean air and normal electrical power. The generator itself can be a small module not much bigger in size than a lecture bottle and either distributed with the gas mixture or provided as part of the test site equipment.

Operation of the generation apparatus would require the provision and attachment of the 2 gas supplies, the plugging in of the electrical supply for the test atmosphere generator, and its attachment to the instrument. The only adjustment which is critical is that determining the flow rate of the dilutent air. It is not expected that the ozonizer would be strongly dependent on the flow rate of the oxygen-containing gas mixture.

After the test atmosphere generator is assembled and turned on, it will require a short period of time, approximately 10 minutes, to stabilize. After this it may remain in operation for 5 or 6 hr without further attention.

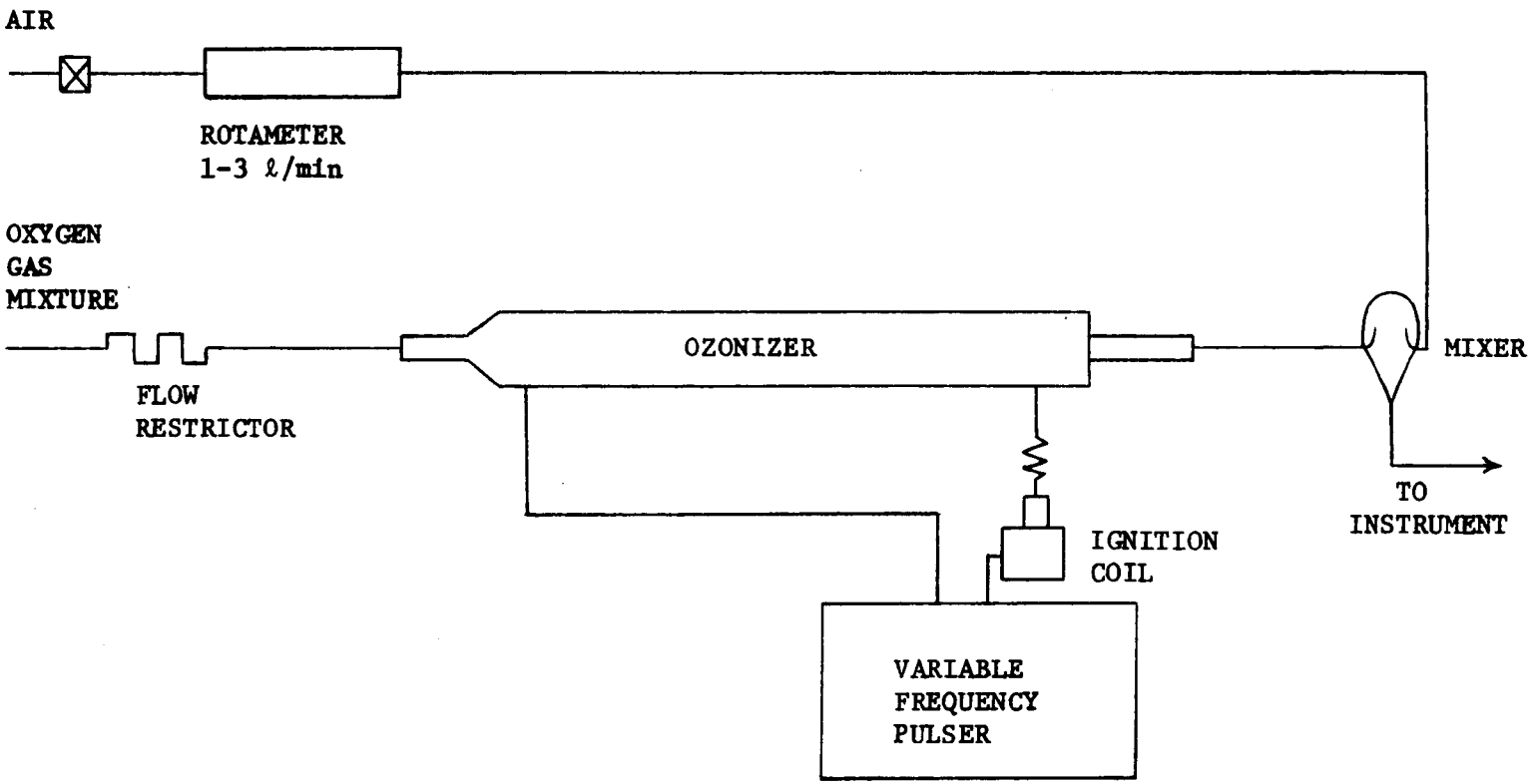


Figure 3-22. Plasma test atmosphere generator for ozone.

D. Maintenance requirements - Aside from preparation of the oxygen mixtures, the generation system required little maintenance. Operating at relatively low input powers, the ozonizer tubes can be expected to have relatively long lives and, properly used, the generation apparatus should not be susceptible to contamination.

E. Shipping requirements - Depending upon the specific test scenario adopted, a given test will require provisions of one lecture bottle containing a gas mixture or alternatively provision of both the gas mixture and the ozonizer which has been preset to a specific plasma energy level.

F. Estimated accuracy - An accuracy of ± 10% should be readily obtainable using the test atmosphere generation system. This could be reduced to 5% or could be as much as 20% depending almost completely on detailed cost-accuracy tradeoffs in the design.

G. Estimated cost - Development cost is estimated to be approximately $50,000. The oxygen-inert gas mixture prepared in sufficient quantities should cost under $5 for each such test atmosphere. The exact cost for the ozonizer depends almost completely upon the design and cost of the ozonizer tube. An estimate of $400 for the generator appears reasonable but would be dependent upon its detailed design, required precision, and number manufactured. It would be required to carry out a development project in order to test the efficacy of this technique and to provide calibration and operational data.

H. Advantages/Disadvantages

Advantages

1. Sample preparation and distribution is relatively easy.
2. A dynamic test atmosphere generator is provided.
3. The generator is relatively independent of operator proficiency.

Disadvantages

1. A development and testing program is required.

I. Design sketch - See Figure 3.22.

J. Recommendations - While a plasma generator for ozone can no doubt be obtained and will operate satisfactorily, it must be compared to the ultraviolet ozone generator for which considerably more experience has

been obtained.

The logistics of this testing technique are more involved than in some others suggested.

K. References

1. F. K. McTaggert, Plasma Chemistry in Electrical Discharges, Elsevier Publishing Co., New York 1967.
2. "Operation and Service Manual for Bendix Model 8101-B Oxides of Nitrogen Analyzer", Bendix Corporation, Ronceverte, West Virginia.
3. A. P. Altshuller and A. F. Wartburg, Intern., J. Air Water Pollution 4 70 (1961).
4. S. Kaye and J. E. Koency, Anal. Chem. 41, 1491 (1969).
5. S. Kaye and J. E. Koency, Rev. Sci. Instr. 40 505 (1969).
6. B. L. Richards, O. C. Taylor, and G. F. Edmunds, J. Air Pollution Control Assoc. 18 73 (1968).

3.3.2.5 Plasma Generation of 1-Butene Test Atmospheres

Similarly to the situation with carbon monoxide, the chemistry of active organic species in a plasma discharge is so poorly controlled as to prohibit a viable approach to a 1-butene test atmosphere generator. In essence, while it may be possible to obtain such a technique, the research cost that would be involved in attaining this capability is prohibitive.

3.3.3 Thin Films of Dissolved Reactants

3.3.3.1 Sulfur Dioxide

A. Principles involved - The same general type of apparatus as is described in Section 3.2.3 can be utilized, except that two solutions would have to be mixed, the reaction generating SO_2. Many of the reactions which generate SO_2 must be heated, so the contact column (See Figure 3.23) would require a water or steam jacket. Solutions to be used could be transported in glass containers and the hydrostatic head could be maintained using an open glass leveling bulb.

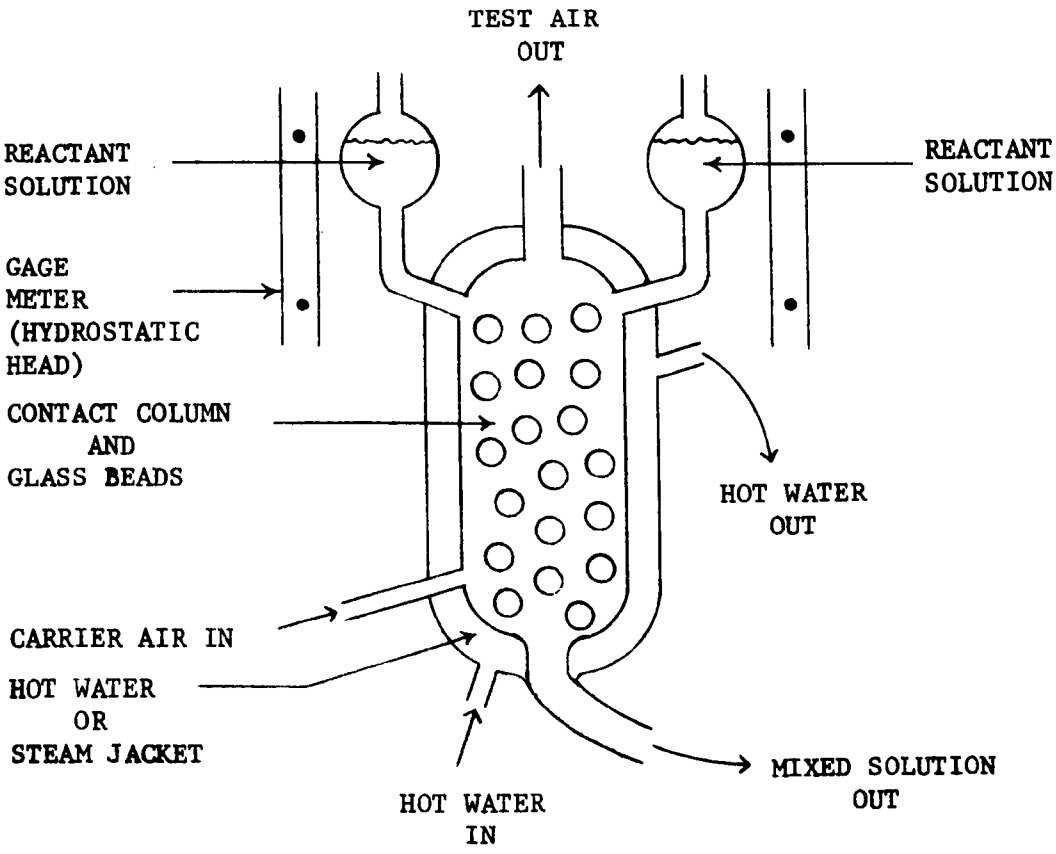


Figure 3-23. Reactant test atmosphere generator.

At about 50 to 100°C a solution of sodium dithionate ($Na_2S_2O_6$) with concentrated acid will produce SO_2. The reaction is:

$$Na_2S_2O_6 + 2H^+ \xrightarrow{250°C} H_2SO_4 + 2Na^+ + SO_2.$$

The acid should be in excess (Ref. 1)

Other reactions may be used, but many are unsuitable because of extreme reaction conditions (e.g., excessive temperature needed).

B. Physical characteristics - Figure 3-23 is a diagramatic representation of such an exchange system. The two solutions would be delivered at a known constant rate. The exact rate of release of SO_2 would best be determined empirically.

C. Operational requirements - Operation should not be too complex. Once the apparatus is assembled:

1. Liquid flow is turned on by opening a valve for each of the solutions with the flow rate controlled by capillary tubes.
2. Air flow would be controlled at the specified rate.
3. When liquid begins to accumulate in the bottom of the contact column the instrument to be tested can start sampling the test atmospheres.
4. Care should be taken to maintain the liquid at the preset level to insure constant solution flow.

D. Maintenance requirements - The device should be cleaned and checked for correct flows before and after field use. Broken parts should be replaced. The whole system should be calibrated in the home laboratory prior to being used in the field. Solutions of reactants would be prepared and analyzed in the home laboratory.

E. Shipping requirements - A case for the apparatus should be rigid, the parts should be strapped in. When shipped the interior should be stuffed with shock absorbant filler of some kind. It's weight should not exceed 6.8 kg.

The reactants should be shipped in inert sealed containers.

F. Estimated accuracy - Delivery of an accurately known concentration of the pollutant depends on measurements in the home laboratory which relate concentration to the various settings of the apparatus and to temperature.

Precision of delivery will depend on control of temperature and the accuracy of the hydrostatic head and the air flow setting. A single point flow meter can help the latter. The hydrostatic head can be designated by fixed marks on a stick, but probably will require frequent adjustment.

G. Estimated cost

Estimated Development costs	$35,000
Supplies - Each test setup	1,000
Each test	25

H. Advantages/Disadvantages - With proper quality control the technique should be adequately accurate and precise. The advantage of this technique over that of using dissolved gases is that no special care need be exercised to prevent the loss of any reactant from solution before mixing in the contact column.

The major disadvantage is that hazardous reactants such as strong acids are needed.

I. Design sketch - See Figure 3-23.

J. Recommendations - This is not too attractive, largely because it is more complex and somewhat more elaborate than many added necessity of having to maintain a constant temperature may also make it less desirable. There is a possibility that this technique could prove attractive, but much development work would be required.

The recommendation is not to develop this technique unless experience shows none other to be completely satisfactory.

K. Reference

1. Kleinberg, J., W. J. Argersinger, Jr., and E. Griswold, Inorganic Chemistry, D. C. Health, Boston, p. 453 (1960).

3.3.3.2 Nitrogen Dioxide

A device for generating a test atmosphere of NO_2 could be constructed exactly as described for SO_2 in the previous section except that the hot water jacket would not be needed.

A solution containing sodium nitrate and sodium nitrite in equimolar concentrations can be mixed with concentrated acid to produce NO_2:

$$NaNO_2 + NaNO_3 + 2H^+ \rightarrow 2Na^+ + H_2O + 2NO_2 \qquad \text{(Ref. 1)}$$

The cost would be similar to that for the SO_2 device. Other considerations will be the same as for the SO_2 device.

Reference

1. Cotton, F. A. and G. Wilkinson, Advanced Inorganic Chemistry, Interscience N. Y., p. 258 (1962)

3.3.3.3 Carbon Monoxide

The same device and the same considerations apply in the case of CO as for SO_2. The chemical reaction at 100°C is between formic acid (H_2COOH) and concentrated H_2SO_4

$$H_2COOH + H_2SO_4 \rightarrow H_2SO_4 \cdot H_2 + CO. \qquad \text{(Ref. 1)}$$

Reference

1. Cotton, F. A. and G. Wilkinson, Advanced Inorganic Chemistry, Interscience, N. Y. p 225.

3.3.3.4 Ozone

No reaction system producing ozone is known to exist.

3.3.3.5 Butene-1

The same considerations hold for Butene-1 as for SO_2 including estimated costs and recommendation. The reaction would be dehydration of butyl alcohol with concentrated H_2SO_4:

$$C_4H_9OH + H_2SO_4 \rightarrow H_2SO_4H_2O + C_4H_8. \qquad \text{(Ref. 1)}$$

Since butyl alcohol also activates FID, a cold trap with suitable refrigerant or an adsorbent of polar components such as ascarite should be placed between the generator and the instrument under observation.

References

1. Whitmore, F. C., Organic Chemistry (Reproduction of 2nd Van Nostrand and Co. Edition 1951) Dover, Inc., New York, p. 39.

3.3.4 Electrochemical Methods

There are two general techniques for employing electrochemical processes in the generation of test atmospheres. The first of these uses the controllable quantitative generation of gases as a driving force for an impurity injection system. This merits careful consideration and is discussed below. The second technique involves the direct generation of the impurity gases in the electrochemical reaction. This depends on the existence of a suitable reaction and is therefore limited in its applicability. No suitable electrochemical reaction of the generation of sulfur dioxide has been identified, however in subsequent sections application of this technique to the generation of ozone and nitrogen dioxide test atmospheres will be described.

The versatility of electrochemical processes and the quantitative relation of reaction rates to the controllable flow of electric current indicates the need for more extensive consideration than is given here. One would like to consider a solid electrolyte-gas generation system for example. Perusal of the literature, however, indicates that phase changes involving gas generation are unstudied. Emphasis has been on reversible electrochemical processes in which no phase change occurs. No data exists on gas generation in such processes. Other potential test gas atmosphere generation methods based on electrochemical processes might be derived from release of entrapped gases in electrodeposited films, by-products of miniature fuel-cells, the release of entrapped pollutant gas by electrochemical dissolution of a metal electrode, or one of the more complex electrochemical processes.

3.3.4.1 Sulfur Dioxide

A. Principles involved - The test atmosphere generation scheme using the electrochemically evolved gases as a driving force is described in this action for sulfur dioxide but is equally applicable to the injection of other impurity gases. In particular it will be referred to as a competitive technique in each of the following sections dealing with electrochemical test atmosphere generators.

Test atmosphere generators based upon use of generated gases as a driving force for injection of impurity gases into a flow stream can take many forms. Gas syringes using electrochemical gas generation as the driving force are available commercially. These are capable of delivering from 0.04-4 ml/hr and can operate for 10 days without recharging the electrolytic cell. They are battery driven.

Since the number of molecules per unit volume of gas is independent of the type of gas, the relationship between the rate of gas generation in an electrochemical cell and the electrical current required does not depend upon the type of gas generated except as that relates to the number of electrons required to liberate one molecule of gas. Assuming 2 electrons are required per molecule as occurs for example with the generation of oxygen, then doping levels from .05 to 5 ppm (130-13,085 $\mu g/m^3$) in gases flowing at rate from 1 to 3 ℓ/min require cell currents in the range from about 7 μA to 2 mA. Since it is inadvisable to operate electrochemical cells below 10 μA when quantitative generation is required, the use of electrochemical cells for impurity injection at the lowest concentration and lowest flow rate would not be advisable. This is a very minor limitation on the operating range.

The most convenient way to provide test atmosphere generation using electrochemical reaction as the driving force appears to be in the form of a small container. The container, about the size of an aerosol paint can, would contain the dopant gas, in this case sulfur dioxide. In the bottom of the can but separated from it by an extensible diaphragm would be placed an electrolytic cell. The diaphragm may actually consist of either an elastic material or a collapsed bag of a selected plastic. The electrolyte need be nothing more than salt water. The electrodes would be brought through the bottom of the can. Upon receipt, the tip of the sealed plastic capillary tube in the top of the can would be broken off and the can attached to the instrument manifold. Using a small constant current power supply or a battery, the electrolytic cell would be energized. The electrolysis gases will expand into the bottom of the can forcing the original contents of the can out through the capillary at a constant rate. This rate could be adjusted from 0.1 to 10 ml/min. It would be possible to adjust the impurity concentration

in the gas by varying the current, by varying the dilutent flow rate, or by varying the dopant concentration in the canned gas.

B. Physical characteristics - This test atmosphere generation device consists of a can of gas, the weight of which should be under one pound and with no dimension greater than 15.2 cm. While a more sophisticated power supply can be employed, it is more convenient to employ a standard dry cell as a source of power for the electrolytic cell. This could require use of a current limiting resistor in order to obtain the accuracy required.

C. Operational requirements - At the test site, the operator would take a can of gas as received and attach it to the intake manifold. In doing this he would break off at a notch the tip of the output tube of the can. After attaching the can to its manifold he would attach wires from a dry cell to the electrodes provided on the can and adjust the flow rate of air through the manifold to a specified standard flow rate. He would then be ready to operate his instruments.

D. Maintenance requirements - There are no maintenance requirements associated with this method of test atmosphere generation.

E. Shipping requirements - There would be no extraordinary or complex shipping requirements associated with the use of canned gas. Pre-filled cans of gas with internal pressure approximating normal atmospheric pressure and containing sulfur dioxide in a preselected mixture will be required. Because of the low pressures, there would be no particular hazards associated with these shipments.

F. Estimated accuracy - Sulfur dioxide mixtures can be provided in the can such that little deterioration would occur. There would be little room for error in attaching a dry cell to the terminals provided on the can, therefore the prime source of error would be in the determination of the flow rate in the measuring instrument manifold. This however is part of the normal operating requirements on the measurement facility and should not be considered as part of the test atmosphere generation inaccuracy. It is estimated that 5% accuracy would be readily obtainable as determined by the can dimensions, filling pressure, temperature, and mode of operation. Temperature equilibration would be required.

G. Estimated cost - It is estimated that the cost of manufacturing and filling a can with a specified SO_2 mixture would be less than $15 per test when quantities on the order of hundreds are required. This cost would include the gas, the built-in electrolytic cell, the separation diaphragm, and provision of a dry battery. The can would be discarded after use. Development costs of $50,000 would not be unreasonable.

H. Advantages/Disadvantages

Advantages

1. This is a simple and readily employable technique with little opportunity for error.
2. The electrolytic injection system exhibits cost advantages.

Disadvantages

1. In order to obtain a variety of concentrations and types of gases it may be necessary to purchase machinery to prepare and seal the cans. More likely a commercial supplier can be identified.

I. Design sketch - The concept of using a canned gas should be given careful consideration because of its logistical simplicity and its relative freedom from error. See Figure 3-24.

3.3.4.2 Nitrogen Dioxide

A. Principles involved - As described in the previous section for sulfur dioxide, nitrogen dioxide can also be provided to a test atmosphere by electrochemical injection. However, nitrogen dioxide is one of the gases which can be supplied as the product of an electrochemical reaction and consideration will be given to this method for providing a test atmosphere. The reactivity of nitrogen dioxide makes this generation technique attractive compared to methods requiring long-time storage.

Nitrogen dioxide cannot be produced directly from an electrochemical reaction. However nitric oxide is generated quantitatively by the electrolysis of nitrosyl hydrogen sulfate ($NOHSO_4$) dissolved in concentrated sulfuric acid at a platinum cathode under an atmosphere of nitrogen. At the same time the anode reaction produces oxygen that, when allowed to mix with the nitric oxide before dilution, provides a quantitative yield of nitrogen dioxide. This same basic process is described in section 3.3.2.2 wherein the nitric oxide is reacted with plasma produced ozone to give quantitative nitrogen dioxide.

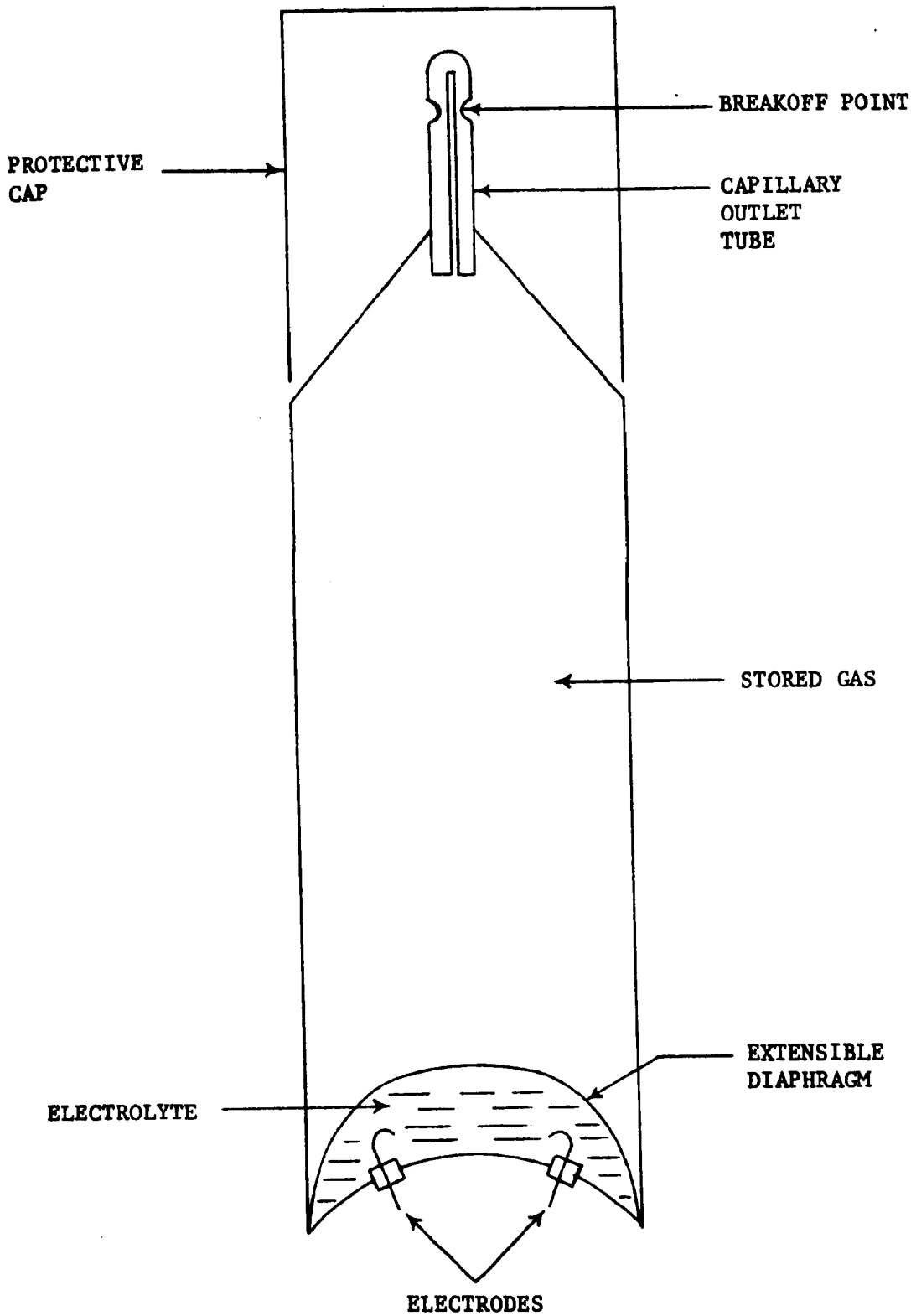


Figure 3-24. Canned dopant gas with electrolytic drive.

In one electrolytic generator nitric oxide from the cathode and the oxygen from the anode were led through a capillary tubing to a mixing bulb where the nitrogen dioxide was formed. The output of the mixing bulb was measured with a nitrogen dioxide analyzer. At 800 μA of cathode current, sufficient nitrogen dioxide was produced to obtain a 12 ppm concentration in a 1 ℓ/min dilutent stream. Experiments indicated that it would be possible to control the nitrogen dioxide production by controlling either nitric oxide or oxygen evolution rates.

B. Physical characteristics - The design of the electrochemical nitrogen dioxide test atmosphere generator will require ingenuity in order that it satisfy the generator requirements. One problem is the low generation rate for nitric oxide (12 μℓ/min) which is required. This must be mixed with the oxygen flow before dilution in order that it be converted to nitrogen dioxide. This means that the cell must have a minimum of dead space or, at the low flow rate, it will require an unacceptable long period of time for the generated gases to replace those in the dead space. Another problem is associated with the handling of the cell. In order that the cell be useful for test atmosphere generation, it must be capable of shipment and handling. This requires that the cell be designed so that the liquid electrolyte will not enter the gas flow system thereby creating barriers to the gas flow and depleting the electrolyte supply.

Some solutions to these problems are evident. For example, in the cell design it is unnecessary to separate the anode and cathode. This would allow the cell itself to serve as the mixing chamber. Provision must be made for the fact that non-stoichiometric quantities of nitric oxide and oxygen are produced.

Ingenuity applied to this design problem should allow the development of a self-contained generation unit which is no more than 15.2 cm on a side and which contains the required cell or cells batteries and other devices as needed. The outlet of this unit when properly attached to an instrument manifold would be capable of supplying nitrogen dioxide test atmospheres over the full range of those required.

C. Operational requirements - An electrolytic nitrogen dioxide generator which is properly designed should operate for a minimum of 10 hr without battery replacement. Replacing the dry cells at regular intervals should allow the generator to be used for 50 or more hrs without regeneration of the electrolyte. The unit would be relatively easy to handle and would require a minimum of operator skills. Optimally, no external supplies of gas or electrical energy would be necessary. It may be advantageous to consider a non-reusable unit.

D. Maintenance requirements - See previous subsection.

E. Shipping requirements - The electrolytic nitrogen dioxide generator is in many respects similar to small laboratory wet cells employed for calibration of electrical equipment. Thus, in a suitable shipping container, they should be able to survive the rigors of transportation without damage and would not be limited in their transportability. The small amount of concentrated sulfuric acid which is contained within the cell would be completely absorbed by the packing material if an accident should occur.

F. Estimated accuracy - In a laboratory environment with ample time for achieving stability, accuracies of better than 5% are readily obtainable with this generator, 1% accuracies have been claimed. In a field test environment, with limited time for achieving stability, accuracies of approximately 10% should be expected.

G. Estimated cost - The largest cost associated with this test atmosphere generation system is that for development. There are a number of laboratory measurements which must be made and the generator design requires considerable effort. A sum of $50,000 could readily be utilized in accomplishing this. Once the design cycle is completed, it would be expected that test atmosphere generators would cost on the order of $30 in small production lots. Periodic cell regeneration should cost no more than $10 per cell.

H. Advantages/Disadvantages

Advantages

1. The electrolytic cell is potentially capable of providing test atmospheres utilizing the flow rates in the instrument manifold such that no additional external gas or energy requirements exist.

2. The basic principle of electrolytic generation of dopants for test atmospheres is its highly quantitative nature which lends itself to accuracy.

Disadvantages

. A considerable development effort is necessary to achieve an acceptable operating generator.

I. Design sketch

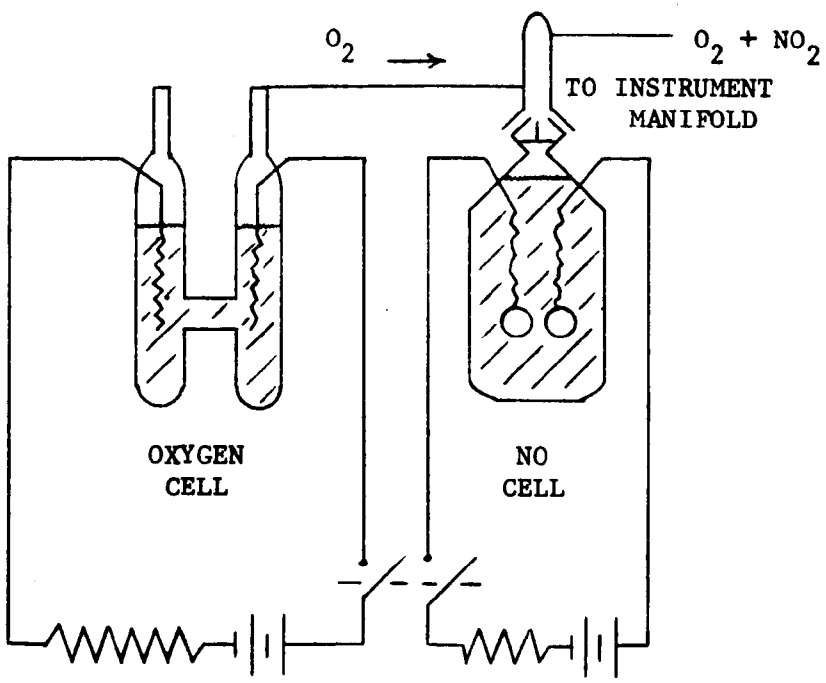


Figure 3-25. Electrolytic test atmosphere generator for nitrogen dioxide.

3.3.4.3 Carbon Monoxide

No electrochemical process has been identified from which carbon monoxide may be derived. Therefore, the only test atmosphere generation

technique which will result in a carbon monoxide test atmosphere is that based upon electrochemical injection as described in Section 3.3.4.1. This involves the provision of a gas mixture containing carbon monoxide in known quantities such that it may be metered into an instrument manifold flow by means of the electrochemical injection system. This utilizes the quantitative evolution of gas to exert a force on an isolated volume of carbon monoxide which is then injected into the flow stream at a known controlled rate.

3.3.4.4 Ozone

The generation of ozone in an electrochemical reaction has been studied extensively. The cell utilizes sulfuric acid as an electrolyte and two platinum electrodes. Hydrogen is evolved at the cathode and a mixture of oxygen and ozone at the anode. This process is however not sufficiently quantitative to serve as the basis of a test atmosphere generator.

Another method for quantitative generation of ozone could be considered based upon quantitative evolution of oxygen from an electrolytic cell and the subsequent plasma conversion of the oxygen to ozone. The efficiency of plasma ozonization is however small and, coupled with the low evolution rate of electrochemical processes, will be an unlikely candidate for an ozone test atmosphere generator.

Barring further research on either of the above two methods, it appears that an ozone test atmosphere generator based upon electrochemical reactions is only possible based on the injection technique described in 3.3.4.1. This would depend upon the provision of ozone in a gas mixture with sufficient concentration and stability to serve as a source for subsequent dilution. Although dilute ozone gas mixtures have been known to be very stable under carefully prescribed conditions (i.e., up to 8 percent ozone), this technique appears to be a second choice which should be considered only if other test atmosphere generation schemes encounter problems. A generator based upon electrochemical injection would be very similar to and have the same general attribute as that described for sulfur dioxide.

3.3.4.5 1-Butene

This non-methane hydrocarbon cannot be evolved from an electrochemical reaction nor can it be derived from gases from such reactions. Complex organic species of this type require more sophisticated synthesis techniques. Thus the only test atmosphere generation scheme utilizing electrochemical reactions which can be applied to 1-butene test atmospheres is that based upon injection as described in Section 3.3.4.1. One must be careful to take into account the condensation of 1-butene at room temperature and moderate pressure.

3.3.5 Films of Laminated Reactants

3.3.5.1 Sulfur Dioxide

A. Principles involved - Laminar films for generation of test atmospheres could include:

(1) Films of Laminar material containing pure pollutant gas.

(2) Films consisting of or containing reactants which would be brought together mechanically in the test atmosphere.

Items (1) and (2) above could be "sandwiches" in which the material of interest is held between inert layers or they could be a layer or layers encapsulated within the body of the inert material.

Mechanically, the most easily delivered and disrupted film might be a paraffin wax with bubbles of pollutant in it. Such a paraffin wax could be obtained or prepared with a desirable melting point, e.g., ~30°C, (C_{16} to C_{20} normal alkanes melt at ~18°C to ~37°C) [Ref. 1]. At a temperature slightly above melting for the alkane wax, the pollutants could be stirred into the wax. The wax could be chilled into a film of convenient thickness, width, and length. Some experience in quality control would allow a fairly uniform product to be made.

The film could be run into a chamber with a warm surface (Teflon covered), the paraffin wax melted at a desired rate, and the SO_2 released.

A temperature of ~30°C would not generate a reaction between the SO_2 and the paraffin wax nor would it cause any other thermal reactions, such as degradation of the pollutant to take place.

Sulfur dioxide at one atmosphere pressure could be stirred or whipped into melted paraffin wax as small bubbles and the material cooled rapidly by being extruded as a thin film into cold water. The pollutant content would, as stated, depend on the condition of preparation.

After mixing, while the wax is still easily malleable it can be rolled into desired dimensions or even shaped into uniform sticks. Alternately solutions could be prepared as films, introduced into the test air, and melted simultaneously. Higher melting wax could be used for the reactions

$$Na_2S_2O_6 + 2H^+ \rightarrow H_2SO_4 + 2\ Na^+\ SO_2 \qquad \text{(Ref. 2)}$$

as it requires a temperature of 50°C or higher.

B. Physical characteristics - The physical characteristics of the system are described above.

C. Operational requirements - The characteristics of movement (films and air) should be determined by the central laboratory, so that only mechanical assembly and setting of control to previously designated readings is necessary by the field operator.

D. Maintenance requirements - Production of paraffin wax films containing known quantities of pollutant, plus quantitative testing of the content must be performed at the central laboratory. Calibration of the heating system must be maintained. Cleaning the apparatus and removing melted wax would be necessary.

Care must be taken in storage and in transit to maintain a cool temperature to prevent melting or undue cold flow of the film.

E. Shipping characteristics - The entire apparatus should weigh 4.5 kg or less (less case) and the case should weigh no more than 6.8 kg. The overall dimensions of the case should be no more than 38.1 x 30.4 x 30.4 cm.

A rigid wooden or metal container and cushioning packing material should be sufficient. Inside the shipping container the wax film should be packed in some insulating material or surrounded by a refrigerant.

F. Accuracy - The accuracy would depend almost entirely on the quality control performed by the central laboratory. The only judgment needed by the field operator would be in setting flow rates of air.

G. Estimated cost and supplies

Zero gas	$60
Sulfur dioxide	15
Material for case	50
Custom glassware	500
Other reagents including wax	60
	685
Equipment	
Heating element	25
RPD motor	30
Heated-blender	90
Flow meter air	50
Gas regulators	430
Ozone generator	190
	815
Service	
Teflon coating	500
Machine shop	150
	650
Development cost	$40,000
Cost of kit	
Gases and chemicals including wax film prepared	20
Zero gas	60
Custom glassware	250
Case	50
Teflon coating	250
	$640

H. Advantages/Disadvantages - If assembly of the apparatus and central laboratory quality control is good, it represents a very simple operation for the field person.

Set air flow desired, turn on constant speed RPD motor and turn on heating element.

I. Design sketch. See Figure 3-26.

J. Recommendations - The development of such a device should be worth pursuing.

K. References

1. Whitmore, F. C. Organic Chemistry (Reproduction of 2nd Van Nostrand and Co. Edition 1951) Dover, Inc., New York, p. 39.
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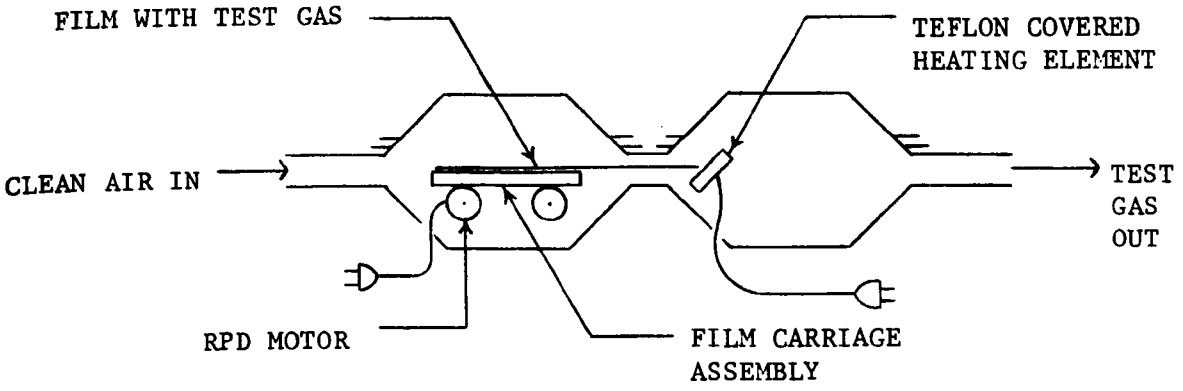

Figure 3-26. Dissolved gas test atmosphere generator.

3.3.5.2 Nitrogen Dioxide

The same considerations including cost and recommendations apply to NO_2 as to SO_2.

If bubbles of solution are used instead of gaseous NO_2, the reactant solutions could be $NaNO_2$ + $NaNO_3$ and a strong acid:

$$NaNO_2 + NaNO_3 + 2H^+ \rightarrow H_2O + 2Na^+ + 2NO_2$$

Reference

1. Cotton, F. A. and G. Wilkinson, Advanced Inorganic Chemistry, Interscience, N.Y. p 258 (1968)

3.3.5.3 Carbon Monoxide

The same design and considerations apply to CO as to NO_2. If reactant solutions are used they could be liquid formic acid and concentrated H_2SO_4 at 100°C:

$$H_2COOH + H_2SO_4 \rightarrow H_2SO_4H_2O + CO \ .$$

Reference

1. Cotton, F. A. and G. Wilkinson, Advanced Inorganic Chemistry Interscience, N. Y. p. 225 (1962).

3.3.5.4 Ozone

The same technique could be used for O_3. This would call for an additional $250 for an O_3 generator. The temperatures involved would not

cause a destruction of O_3. The partial pressure of O_3 in the entrapped bubble would be only of the order of 0.01 atm.

No thermal reactions of liquids or solutions are known to generate O_3, so the alternative is not open for the production of a test atmosphere containing O_3.

3.3.5.5 Butene-1

Butene-1 might dissolve in the paraffin wax, but the technique should be a valid one for producing a butene-1 test atmosphere. The same considerations apply as for the SO_2 system.

If the alternate system of generating butene-1 from two reactant solutions is desired the reactant would be liquid butanol and concentrated H_2SO_4:

$$C_4H_9OH + H_2SO_4 \rightarrow H_2SO_4H_2O + C_4H_8 \ .$$

providing any excess butanol is removed by condensation on adsorption.

Reference

1. Whitmore, F. C., Organic Chemistry (Reproduction of 2nd Van Nostrand and Co. Edition 1951) Dover, Inc., New York, p. 4.

3.4 Biological Generation

The metabolic diversity of biological systems and the application of biological processes to the production of various hydrocarbons encourages the consideration of such processes for test atmosphere generation. The practicality of application restricts consideration to microbiological organisms of which there are many. Micro-organism may be found that attack all forms of organic matter as well as some inorganic matter. In examining the many products of such reactions, only a few are found that offer potential in test atmosphere generation.

3.4.1 Sulfur Dioxide

Many biological systems are capable of producing sulfite ions as an intermediate during sulfur and sulfate metabolism. However, none have been reported in the literature that are capable of producing gaseous sulfur dioxide.

3.4.2 Nitrogen Dioxide

Similarly to sulfur dioxide, the synthesis of the NO_2^- ion is also commonly found as an intermediate in nitrogen metabolism but the production of nitrogen dioxide has not been reported.

3.4.3 Carbon Monoxide

A. Principles involved - Biological production of carbon monoxide (CO) has been reported in bacteria (Ref. 1,2), yeast (Ref. 1), algae (Ref. 3-8), fungi (Ref. 1,9), higher plants (Ref. 10,11) in siphonophores (Ref. 12) and in man (Ref. 13,14). It is well established that during the catabolism of hemoglobin in senescent erythocytes in human beings, the heme ring is cleaved by removal of the α-methyne bridge carbon, which is then oxidized to CO. Recently, it has been reported that during formation of phycocyanobilin, equimolar quantities of CO are similarly produced (Ref. 15). Phycocyanin is produced by the unicellular alga Cyanidium caldarium. If the alga is grown in the dark, it lacks the photosynthetic pigments but synthesizes chlorophyll a and phycocyanin when placed in the light producing 1 mole CO for each mole of pigment. The proposed technique for generating CO as a test gas for field use is based upon the above phenomenon.

The amount of CO produced is a function of the number of cells of Cyaniduim caldarium. The number of moles of CO produced is directly related to the rate of phycocyanobilin synthesis in C. caldarium. The rate of phycocyanobilin synthesis can be determined spectrally (Ref. 15); thus the CO rate is also known.

C. caldarium cells are grown in the dark in a MF 114 New Brunswick fermentator to yield about 140 g fresh weight. The cell suspension is aereated with 95 percent 0_2 - 5 percent CO_2. The alga is illuminated (light intensity to be experimentally determined) during which time phycocyanobilin and CO are produced. The cells are harvested and resuspended in new media. The cell density and phycocyanobilin content are determined spectrally and a known number of cells are placed in a glass generating system to yield known desired rates of CO. The gas reservoir (headspace) is purged with compressed air at rates to yield the final desired CO/air mixture.

B. Physical characteristics - An algal cell culture as described has been reported to produce CO up to 72 hr after illumination has begun (Ref. 6). Thus, it is proposed that CO generation be initiated at the laboratory site. The generating system is then transported to the field within these time frame conditions. The CO/air mixture should be scrubbed to remove CO_2 using a Baralyme or Ascarite cartridge.

The physical parameters of this system are estimated as follows:

Weight

Glass culture container - (with media	11.3
Illuminating lamps -	1.4
Mixing device -	2.3
Compressed air bottle - (serves also as aereator for culture)	2.3
Teflon storage bag	0.2
Precision valve and tubing	0.2
Total weight	17.7 kg

Unit Dimensions

Stirrer motor	7.6 x 10.1 cm
Air lecture bottle	38.1 x 5.1 cm
Culture container	15 ℓ capacity

Total dimensions: 61 x 61 x 91 cm

C. Operational requirements - If the continuous delivery of CO is found to be feasible from these algal cells, then the unit will require a light source for illumination of the cells, a mixture motor for stirring the cells, and the maintenance of a constant temperature in the culture medium. Adjustment of the vessel purge rate would provide a range of concentrations of CO/air mixtures.

D. Maintenance requirements - The following maintenance is required:

Compressed air bottle. Refill.

CO-generation vessel. Cleaned and replenished with new culture of cells

Storage bag. Flush after using.

Other. As deemed necessary from development studies.

E. Shipping requirements - The vessel should be constructed so as to prevent shattering. Constant illumination is required during transport DC power provided). This method requires an airtight generating system.

F. Estimated accuracy - The accuracy of this method is unknown so it must be determined experimentally; 10 percent should be possible.

G. Estimated cost

(1) Development

Cell fermentator	$1,000
Lamps	100
Algal cells	100
Plumbing and bag	100
Zero air bottle	150
Development	35,000
Total	$36,450

(2) Production

Estimate of $200 per cell plus $50 per test.

H. Advantages/Disadvantages - This should be simple to operate in the field, requiring no prior startup in field operation since generation is initiated in the laboratory. Calibration will be done in the laboratory. The method requires experimental development and verification.

I. Design sketch.

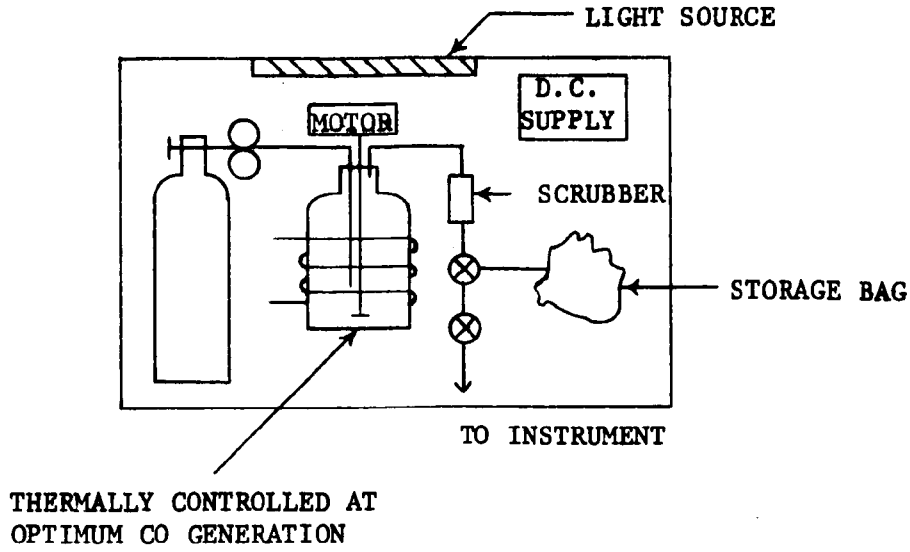

Figure 3-27. Biological test atmosphere generator for carbon monoxide.

J. Recommendation - This method requires considerable experimental development to determine feasibility but may ultimately be a competitive method.

K. References

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3.4.4 Ozone

There is no recorded method by which ozone is produced in a biological process.

3.4.5 1-Butene (Nonmethane Hydrocarbon)

No biological method is known for the production of 1-butene in a biological process but if the objective is to obtain test atmospheres of nonmethane hydrocarbons, then a process is available. Ethylene is the gas and it is available from an enzyme reaction.

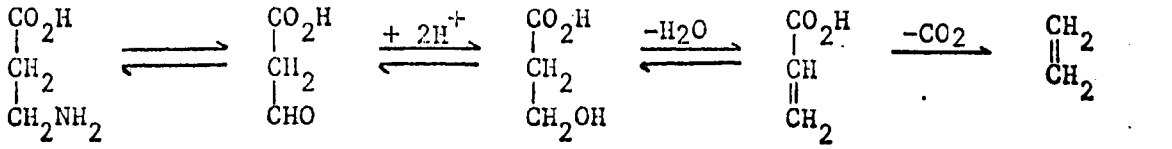
A. Principles involved - Plants readily produce ethylene; e.g. bean cotyledons, apple tissue, pea stems, green bananas, and cauliflower florets (Refs. 1-5). Several investigators have examined possible immediate precursors for ethylene, including methionine, methional, propanol, acetaldehyde, and β-alanine (Refs. 6-8).

Thompson and Spencer (Refs. 9,10) provided evidence which supported the idea that β-alanine was indeed the precursor responsible for ethylene production in bean cotyledons. Subsequently, Stinson and Spencer (Ref. 11) reported the preparation of a soluble enzyme system from the subcellular particulate fraction of wax bean cotyledons which produces ethylene using β-alanine as a substrate. The test generating system proposed here is based upon their enzymatic method (Ref. 11).

1. Principles of enzyme chemistry - The generation of ethylene for use as an atmospheric test gas will be based upon a soluble enzyme system isolated from bean cotyledons. It is appropriate here to review

the basic enzyme reactions responsible for synthesis of ethylene as well as some enzyme chemistry prior to outlining the method proposed for field use.

Ethylene has been shown to evolve from the following enzymic reactions:



β-alanine | Malonate semialdehyde | β-hydroxy propionate | acrylate | ethylene

The enzymes react chemically with the substrate (β-alanine) in the first of a sequence of reactions which ultimately regenerate the enzyme and yield the products. In this sense the enzymes are catalysts. The enzymes are accordingly reacting molecules and their concentrations influence the reaction rate in the same manner as that of the substrate. Therefore, as the enzymes concentrations are increased, the rate of reaction also increases (Figure 3-28).

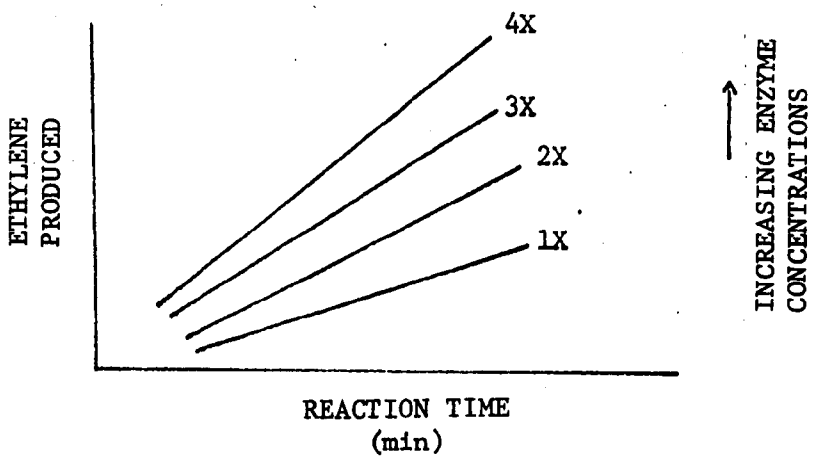


Figure 3-28. Effect of enzyme concentrations on reaction rate, assuming substrate concentrations at saturation amounts.

It follows that this relation can be expressed as

$$\text{Rate} = \frac{\text{Product Concentration}}{} = KE$$

or

$$E = \frac{[P]}{Kt}$$

where E is the enzyme concentration, K is a constant of proportionality, and the reaction rate is measured and expressed as the amount of product [P] formed per unit time, t.

The enzyme concentration is therefore directly proportional to the amount of product formed when all other conditions are held constant. For example, if 0.2 μg/hr of ethylene is produced in one experiment and 0.6 μg/hr in another, the second experiment involves three times as much enzyme. Furthermore, the rate of reaction for enzymes can be expressed in terms of specific activity which is the number of mmol of product produced per unit time per mg of enzyme (S.A. = mmol ethylene/hr/mg enzyme). On this basis calibrated amounts of ethylene can be produced by knowing the S.A. of the enzyme and using the desired amount (weight) of enzyme at the saturating amounts of substrate.

Several other factors affect enzymic reaction rates. As the temperature is raised, the reaction rate of the enzyme reactions increases until a maximum is reached (Figure 3-29).

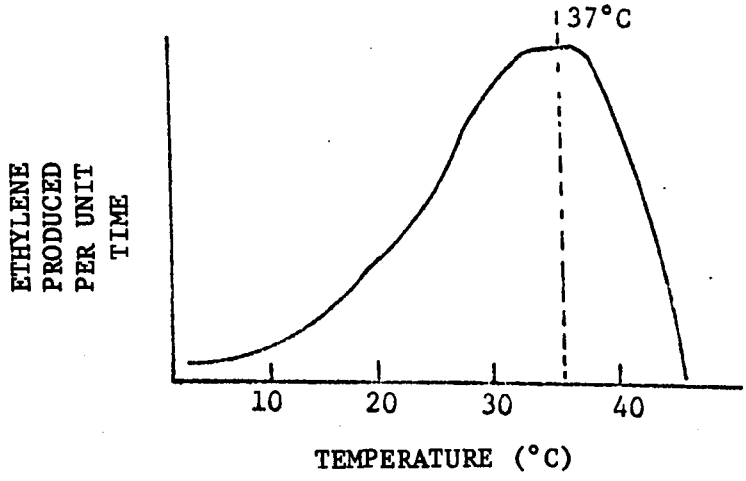


Figure 3-29. Effect of temperature on reaction rate for enzymes.

The temperature coefficient (Q_{10}) for an enzymic reaction is approximately 2; that is, the reaction rate is doubled for each 10°C increase in temperature until a maximum rate is reached. The maximum is usually at 37°C; higher temperatures denature the enzyme and the rate decreases. The apparent temperature for maximum reaction rate is greatly influenced by other experimental conditions.

The hydrogen ion concentration of an enzyme solution also has a marked effect on reaction rate (Figure 3-30). This involves a change in the degree of ionization of functional groups at the active site of the enzyme. The enzymes display the greatest activity for ethylene evolution in a solution at pH 7 which presents the greatest percentage of the molecules in the above sequence in the proper ionic form.

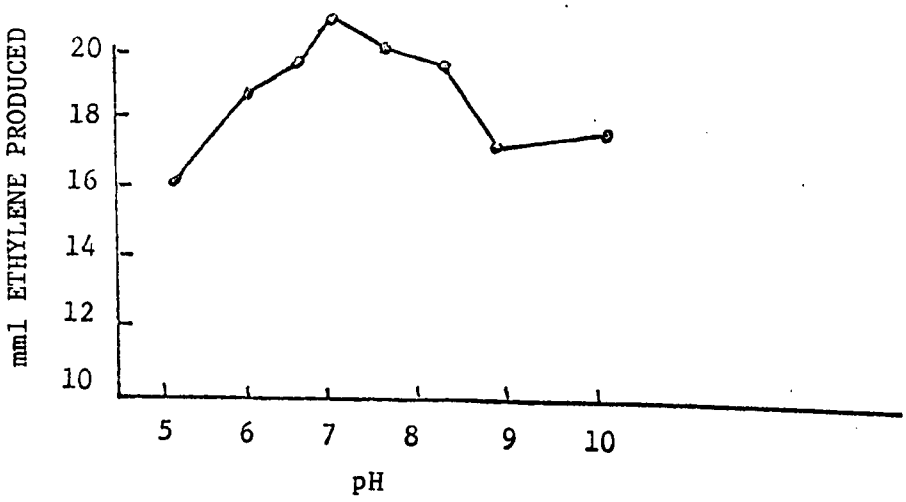


Figure 3-30. Effect of pH on ethylene production.

Another factor that affects enzymic activity (reaction rate) is addition of compounds called cofactors. The addition of $MgCl_2$, pyridoxal phosphate, or thiamine pyrophosphate will enhance catalytic activity and give greater rates of ethylene production. Cofactor (and substrate) are generally supplied at constant optimum concentrations for enzymes. Thus, the reaction rate is controlled primarily by the amount of enzyme present.

Finally, the last important parameter affecting reaction rates is substrate (β-alanine) concentration. With a constant enzyme concentration, an increase of substrate produces at first a very rapid rise in reaction rate (Figure 3-31). As the substrate, β-alanine concentration continues

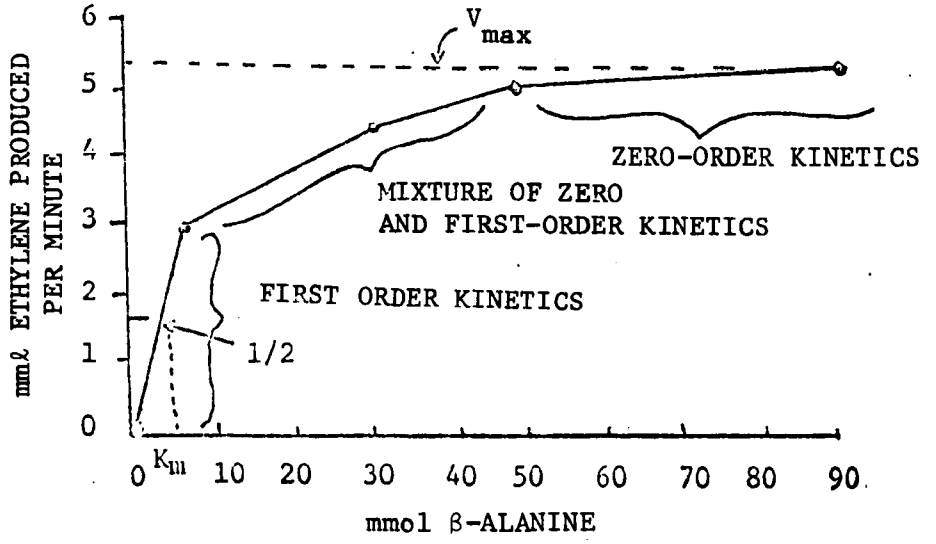


Figure 3-31. Substrate vs product profile at constant enzyme concentration.

to increase, the rate of reaction begins to slow down until with a large substrate concentration, no further change in rate (zero-order kinetics) is observed. This reaction rate at this substrate concentration is defined as the maximum velocity, V_{max}, of the enzyme-catalyzed reaction for ethylene under constant ethylene is constant and controlled solely by enzyme availability.

2. Experimental parameters - This section describes the preparation of materials that are required for a system of producing ethylene as a test atmospheric gas in the field.

In order to obtain cotyledons containing the enzymes for ethylene production, seeds of Phaseolus vulgaris l. var. Kinghorn wax are planted in horticultural grade vermiculite and grown at 26°C in the dark. Cotyledons are picked 4-9 days (should be experimentally determined) after planting.

The enzyme fraction for ethylene production is prepared by grinding cotelydons in a mortar containing 2 ml buffer/g cotyledons (buffer TES = 0.05M N-tris-(hydroxymethyl)methyl-2-aminoethanesulfonic acid) at 0°C. The brei is filtered through cheesecloth and the filtrate is subjected to differential centrifugation. The supernatant from the first spin at 2500 x g for 10 min is again centrifuged at 32,000 x g for 15 min. The pellet formed is resuspended in 0.01M TES, pH 7.6 at 0° and then freeze-dried. The lyophilized fraction is used for ethylene production.

The production of ethylene occurs when the following are all mixed:

(a) TES buffer (optimum pH for activity) is added to a known weight of lyophilized enzyme which will produce the desired rate of ethylene (based on S. A. which is experimentally determined for a batch of enzyme).

(b) Specific Concentrations of Cofactors (ATP, Mg^{++}, Pyridoxal PO_4, Thiamine pyrophosphate) are added to the enzyme solution.

(c) Temperature is brought to 37°C.

(d) The reaction is started immediately upon the addition of an excess of substrate-β-alanine.

B. Physical characteristics - The calibration output requirement for ethylene should be as high as 1 ppm with a constant generating system delivering the sparged air at 3 ℓ/min (maximum rate) for up to 2 hr. The maximum volume of test gas (360 ℓ) would require a total of 360 μℓ of ethylene. Thus, the rate of ethylene evolution should be 3 μℓ/min. Based upon these criteria, the weight of lyophilized enzyme to use would be a direct function of the S. A. of the enzyme (mmol ethylene produced/min/g enzyme).

At the test site, a supply of zero grade air (or inert gas) is required to dilute the ethylene to the final desired concentration. The compressed air may be an integral part of the portable system. The air should be scrubbed of CO_2 and H_2O resulting from the purging of the ethylene generating vessel. This could be done after the test gas has been diluted to the appropriate concentration by employing in tandem cartridges of Lithasorb ($-CO_2$) and "drierite" ($-H_2$)).

The portable generating system conceptually consists of:

		Weight (kg)
(1)	Zero air lecture bottle	2.3
(2)	Lyophilized enzyme, buffer, cofactors, container	2.3
(3)	Valve and tubing	0.2
(4)	Storage container for synthetic ethylene/air mixture (teflon bag)	0.5
	Total weight	4.8 kg

Total Unit Dimensions: 61 x 45.7 x 15.2 cm.

C. Operational requirements - In order to generate the ethylene at a constant rate, its generation would involve adding measured volumes of buffer and cofactors to a closed glass container at 37°C containing a known weight of lyophilized enzyme. The mixture would have to be gently stirred throughout the test period. The surface of the generating solution would be purged with air (or inert gas as desired) at a calibrated fixed flow rate (controlled by a precision valve) to yield the final synthetic air/ethylene mixture. The sparged effluent would be transported directly to an instrument manifold or a teflon storage bag. The system would require a heating jacket to maintain the enzymic generating system at optimum temperature for ethylene evolution (~37°C).

D. Maintenance requirements - Maintenance is required as follows:

(1) Compressed gas bottle. Refilled

(2) Glass ethylene generating system. Washed and dried

(3) Enzyme powder. Prepared in capsular form containing known desired amounts for ethylene production at known rates

(4) Cofactors. Fresh solutions prepared, must be refrigerated prior to use at 0°C.

(5) Other. As deemed necessary from experimental development.

E. Shipping requirements - Cofactors need to be refrigerated.

F. Estimated accuracy - The ethylene enzymic generating system should produce it at a rate within ± 5 percent of desired amount. The overall reproducability and accuracy could be ± 10 percent or less but requires experimental conformation.

G. Estimated cost

Initial development

- Compressed gas plus precision valve and plumbing	$300
- Cofactors (ATP, NADH, Thiamine pyrophosphate, pyrrdoxal phosphate)	1,200
- Seeds of Phaseolus vulgaris	50
- Development	40,000
Total	$41,550

Production

Estimated to be $300 per unit plus $50 per test.

H. Advantages/Disadvantages - This generator should be simple to operate in the field. Large batches of lyophilized enzyme can be prepared and employed for many tests.

There is a possible variability in the S.A. of enzyme preparation with time (over 12 month period) or from batch to batch. After each batch is produced, S.A. would have to be determined experimentally in the laboratory (by GLC) for the rate of ethylene production per mg of lyophilized enzyme powder. Thus, initial calibration is required. Variability of enzyme storage must be determined during experimental development.

I. Design Sketch of Portable System

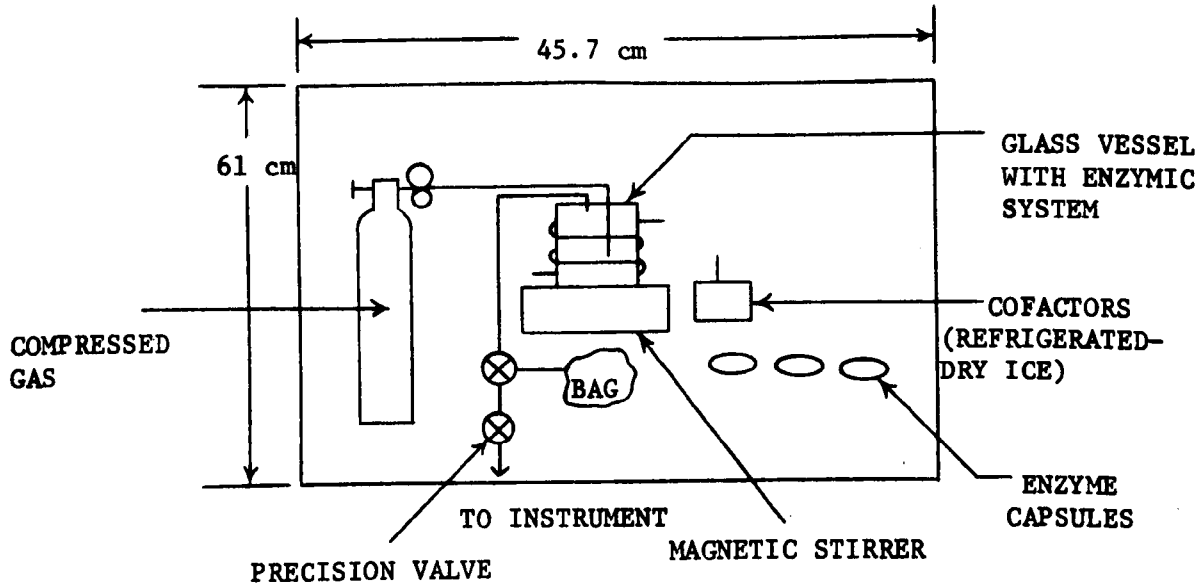


Figure 3-32. Enzyme test atmosphere generator for ethylene.

J. Recommendations - This method should be subjected to more careful searching before undertaking a development effort.

K. References

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3.5 OTHER METHODS

In the preceding paragraphs, one specific method is discussed for each pollutant for each class of methods. As pointed out in Section 2.2, no one classification system can accomodate the varied methods which can be proposed. Even within the classification system employed, a method may be presented which is superior by certain criteria but there may exist other methods which are better by other criteria. This section includes methods not previously described due to the above reasons but which must be considered to assure comprehensiveness.

3.5.1 Foamed Plastic

Expanded plastics are employed for many common applications--packing material and insulation are prominent examples. In these a relatively inert material such as polyethylene is fabricated with numerous air cells resulting in a structually strong form which has a very low density when compared to the unexpanded material. It is suggested that if an appropriate mixture of air and a pollutant gas is employed to form the expanded structure then reproducibility could be obtained in the gas mixture contained in the material. If then, the material is mechanically crushed, the gas mixture would be released for generating a test atmosphere.

To apply this concept, apparatus would be required to form the expanded plastic. The expanded form could be a continuous strip of the material which would contain a calibrated releasable amount of pollutant per unit length. It would be released by crushing. For a dynamic test atmosphere generator, this could be accomplished with a motor operated roller.

This method while appealing from a cost and simplicity viewpoint would have to be tested. The stability of the pollutant mixture in the plastic matrix, the degree of control in the release rate, and other parameters would have to be examined before it could be applied to test atmosphere generation.

3.5.2 Microsyringe

Very small quantities of gases are injected into chromatographic columns and other analytical instruments using calibrated microsyringes. Sample sizes of fractions of a microliter may be injected and motor driven constant rate syringes are available. Thus, it is a simple procedure to provide an appropriate gas mixture that can be withdrawn from a container through a septum and injected through another system into an instrument manifold. Through choice of the pollutant concentration being injected, almost any test atmosphere concentration can be obtained with sufficient accuracy. The only apparent problems are associated with the cost of the syringe and accessories and the design of the generation system so as to minimize operator errors.

3.5.3 Burn Stick

Various pyrolysis methods are adaptable to the use of a burn stick in test atmosphere generation. Using, as an example, the generation of an SO_2 test atmosphere, a suitable slow burning fuse or burn stick may be impregnated with a suitable sulfur compound. With a slow controlled burn rate, in an air stream, the sulfur is oxidized in the combustion to give SO_2 at a predetermined rate.

Slow burning fuses are available and provide sufficient temperature to oxidize sulfur. The primary problems are associated with the production of other gases in the combustion process. Various pollutant levels in the test atmosphere can be obtained by control of burn rate and the chemical concentration in the stick. In operation, the prepared stick in a suitable holder would be ignited and inserted through a port into the air stream in the instrument manifold. It would be designed to burn for the required period. This method is suited to SO_2 and may be possible for NO_2 and CO.

3.5.4 Bubbler Systems

Control of low concentration gas mixtures has been achieved using bubblers in laboratory applications for many years. In brief, the flow of

a gas or gas mixture is controlled by employing a fine valve to release gas through an opening into a non-reactive liquid such that uniform size bubbles are obtained. The bubbles travel up through the liquid at a rate dependent on bubble size and liquid viscosity and are released into the air flow above the liquid. Measuring the size of the bubbles immediately before they escape and the rate at which they are released provides the flow rate for the gas.

While it is easy to obtain dilution factors of 1 part in 10^3 or better in a bubbler system, provision must be made for thorough mixing in the gas stream because of the non-continuous supply of the pollutant gas. One must also be aware of the solubility of the gases in the liquid used; it should be low in order to avoid errors.

There is no doubt that a bubbler dilution system can be employed for test atmosphere generation of some of the five pollutants. There may be difficulty in using it with ozone because of the stability problem. It does require a supply of a gas mixture containing the pollutant gas and is thus a dispensing system.

The same operation can be obtained with a rotating stopcork which releases one stopcork bore volume for each turn.

3.5.5 Exponential Dilution

If a predetermined amount of pollutant is released, perhaps by crushing a vial, into a fixed volume of air and clean air flow into the volume at a known fixed rate while polluted air flows out at the same rate, then the concentration of pollutant in the effluent decreases from a high known initial concentration at an exponential rate. This rate is given by

$$C = C_o \exp\left(-\frac{Ft}{v}\right)$$

where

- C is the concentration at time, t
- C_o is the initial concentration
- F is the flow rate
- v is the volume

Vials of SO_2, NO_2, CO, or C_4H_8 mixtures could be readily prepared for this method and the apparatus and operation of the system could be simplified by design to obtain reliable performance. This system can be made to work and has a number of advantages.

4.0 COMPARATIVE EVALUATION

4.1 Selection of Panel

A panel was selected for the purpose of examining the attributes of the various proposed methods for generation of test atmospheres and to recommend based on the results of the evaluation technique to be presented in Section 4.2, the candidate method for generation of each pollutant gas (i.e., SO_2, NO_2, CO, O_3, and 1-butene). Panel members were selected to bring together individuals with expertise in the fields of physics, chemistry, engineering, and air pollution. The panel members were as follows:

1) Dr. Raimond Liepins (Research Triangle Institute) - Analytical Chemist

2) Dr, L. K. Monteith (N. C. State University) - Professor of Electrical Engineering

3) Dr. L. A. Ripperton (Research Triangle Institute) - Air Pollution/Atmospheric Chemist

4) Dr. R. M. Burger (Research Triangle Institute) - Physicist

5) Mr. C. E. Decker (Research Triangle Institute) - Air Pollution Chemist

4.2 Evaluation Technique

To assist the members of the review panel in the comparison of and ultimately the choice of recommended methods for the generation of the required test atmospheres, summary tables of the fifty methods were prepared and a methods ranking system developed with the special constraints of the project in mind. A summary of eleven methods is presented in Tables 4-1 through 4-5 for each pollutant and contains a brief description of each method. The ranking system developed for the comparative evaluation is presented in Table 4-6 and includes the methods evaluation criteria described in Section 2.1 (Table 2-1) for field usable test atmosphere generating methods, as well as other constraints deemed pertinent to the requirements for which the device/devices were to be used. Briefly, these criteria include the following: simplicity of method; equipment/processing requirements; operator skill requirements; portability

TABLE 4-1. SUMMARY OF METHODS -- SULFUR DIOXIDE

Class	Method #	Description
Contemporary	1	Conventional permeation tube
Desorption	2	Heating of loaded adsorption tube with subsequent dilution
Effusion	3	Low constant pressure can using Freon with calibrated capillary dispenser
Thin film evaporation	4	Column desorption from CCl_4 solvent with carrier gas
Novel permeation	5	Perforated metal-polymer permeator
Photolysis/thermolysis	6	Thermolysis of irridium complex with dilution
Plasma	7	Polysulfide impregnated filter paper in RF discharge containing oxygen
Reactive films	8	Column reaction of liquid films of sodium dithronate with sulfuric acid
Electrochemical	9	Electrolytic generation of gas to obtain calibrated dispensing rate for gas mixture
Laminated reactants	10	Paraffin wax containing SO_2 bubbles
Biological	11	No method recommended

TABLE 4-2. SUMMARY OF METHODS - NITROGEN DIOXIDE

Class	Method #	Description
Contemporary	1	Gas-phase titration of NO from calibrated source with ozone
Desorption	2	Carrier gas through loaded adsorption tube with subsequent dilution
Effusion	3	Low constant pressure can using Freon with calibrated capillary and on-off valve
Thin film evaporation	4	Column desorption from 1,3,5-tioxane solvent with carrier gas
Novel permeation	5	Perforated plate-polymer permeator with perfluoro materials
Photolysis/thermolysis	6	Thermolysis of irridium complex with dilution
Plasma	7	Mixing of electrolytically generated NO with plasma generated ozone
Reactive films	8	Column reaction of liquid films of sodium nitrate and sodium nitrite with acid
Electrochemical	9	Electrolytic $NOHSO_4$ cell and NO + O reaction
Laminated reactants	10	Paraffin wax containing sodium nitrate, sodium nitrite, and acid bubbles.
Biological	11	No method recommended

TABLE 4-3. SUMMARY OF METHODS - CARBON MONOXIDE

Class	Method #	Description
Contemporary	1	Calibrated gas mixture
Desorption	2	Carrier gas through loaded adsorption tube with subsequent dilution
Effusion	3	Variable pressure can with metering valve
Thin film evaporation	4	Column desorption from CCl_4 solvent with carrier gas
Novel permeation	5	Perforated plate-polymer permeator using poly (dimethylsiloxane)
Photolysis/thermolysis	6	Thermolysis of irridium complex with dilution
Plasma	7	Reduction of CO_2 in plasma
Reactive films	8	Column reaction of liquid films of formic acid and sulfuric acid
Electrolytic	9	Electrolytic generation of gas to obtain calibrated dispensing rate of gas mixture
Laminated reactants	10	Paraffin wax containing bubbles of formic acid and sulfuric acid
Biological	11	Algal cell

TABLE 4-4. SUMMARY OF METHODS - OZONE

Class	Method #	Description
Contemporary	1	UV generator referenced to KI
Desorption	2	Carrier gas through calibrated adsorption tube loaded with ozone on silica gel
Effusion	3	None recommended
Thin film evaporation	4	Column desorption from CCl_4 solvent with carrier gas
Novel permeation	5	No method recommended
Photolysis/thermolysis	6	UV photolysis (conventional)
Plasma	7	Plasma ozonizer tube
Reactive films	8	No method recommended
Electrolytic	9	No method recommended
Laminated reactants	10	No method recommended
Biological	11	No method recommended

TABLE 4-5. SUMMARY OF METHODS - 1-BUTENE

Class	Method #	Description
Contemporary	1	Dilution or permeation tube
Desorption	2	Carrier gas through loaded adsorption tube with subsequent dilution
Effusion	3	Lecture bottle with fine metering valve
Thin film evaporation	4	Column desorption from solvent
Novel permeation	5	Perforated-plate polymer permeator
Photolysis/thermolysis	6	Thermolysis of n-iodobutane
Plasma	7	No method recommended
Reactive films	8	Column reaction of liquid films of butyl alcohol and sulfuric acid
Electrolytic	9	Electrolytic generation of gas to obtain calibrated dispensing rate for gas
Laminated reactants	10	Wax containing bubbles of butanol and sulfuric acid
Biological	11	Enzyme generation of ethylene as an alternative to 1-butene

TABLE 4-6. METHOD RANKING SYSTEM

1) Simplicity of Method

- A Relatively uncomplicated
- B Moderate
- C Complex

2) Equipment/Processing Requireemnts

- A Minor requirements
- B Moderate requirements
- C Complex requirements

3) Operator Skill Requirements

- A Low
- B Moderate
- C High

4) Portability

- A Unique requirements for test weight under 2 kg
- B Unique requirements for test weight 2 to 20 kg
- C Unique requirements for test weight over 20 kg

5) Cost

Development		Apparatus		Per Test	
A	Under $20,000	A	Under $100	A	Under $10
B	$20,000-$50,000	B	$100-$500	B	$10-$30
C	Over $50,000	C	Over $500	C	Over $30

6) Safety

- A No obvious safety problem
- B Moderate hazards present
- C Specific safety precautions required

7) Range

- A Full test range capability
- B Perhaps full test range capability but some uncertainty
- C Partial test range capability

TABLE 4-6. METHOD RANKING SYSTEM (Cont'd)

8) Blind Mode

- A Capable of full blind mode operation
- B Subject to operator compromise
- C Incapable of blind mode operation

9) Accuracy

- A Error $\leq$ to 5 percent
- B Error 5 to 10 percent
- C Error 10 to 20 percent

10) Ease of Implementation

- A Ready for assembly and use
- B Requires development, but principles proven
- C Depends on unproven principles

11) Confidence of Success

- A High
- B In between
- C Low

12) Maintenance

- A Little
- B Moderate
- C Much

13) Operational Capability

- A Dynamic (Continuous)
- C Batch

Weighting Factor

A = 4

B = 3

C = 2

of equipment required for method; cost (development, apparatus, per test); safety; range; capability for blind mode of operation; estimated accuracy; ease of implementation; confidence of success; maintenance requirements; and operational capability. Each of the selected criteria was assigned an equal weight in the ranking system for comparison of methods. Usually, three ranks are included as A, B, or C for each of the thirteen criteria selected and are assigned a numerical factor of 4, 3, and 2, respectively. In cases where only two ranks are used, A and C are used with the same numerical values. The criteria and rank descriptions become obvious upon examination of Table 4-6 and will not be further discussed. The utilization of the methods ranking system to select the recommended method for each pollutant is further described in Section 4.3 (Panel Study). Use of the methods ranking system should result in the selection of the best method or concept for generation of test atmospheres at field locations. This statement is based solely on the assumption that the selection criteria and constraints imposed are correct for this application. It is also assumed that an external source of diluent air is available or will be provided at each field location.

4.3 Panel Study

The panel met on December 14, 1973 to examine in detail the fifty discussions prepared for the generation of test atmosphere at field locations. The panel discussion began with a statement of the objective of the project, which was to examine various classes of physical, physical plus chemical, and biological methods applicable to devices for generation of test atmospheres for use in assessing instrument/operator performance. The constraints and requirements applicable to such a quality assurance program were reviewed. The panel meeting continued with a brief discussion of each class of methods (i.e., physical, physical plus chemical, and biological) with particular emphasis being given to advantages, disadvantages, and cost trade-offs for each method within the three classes. Technical aspects, regarding the theory of operation, were reviewed and practical considerations such as the relative merits of each method were discussed.

After completion of the discussion session, the evaluation technique designed to obtain a consensus opinion for the recommended method for generation of each test atmosphere was presented and discussed. Basically, the evaluation procedure consisted of a ranking system based on numerical considerations for the thirteen sets of criteria previously described in Section 4.1. Five work sheets identical to that shown in Table 4-7 were distributed to each panel member, along with a summary of methods (Section 4.1 - Tables 4-1 to 4-5) and the methods ranking system (Table 4-6). Each of the thirteen sets of criteria were reviewed by the panel and discussed. In several cases pertinent comments were raised regarding the criteria and constraints presented for the methods ranking system. These comments were reviewed, modified as needed, and a consensus set of criteria developed. These criteria are identical to those presented in Table 4-6. For the most part few revisions were necessary. Each panel member was then requested to review, in detail each of the fifty discussions and to complete the five tables needed to obtain a consensus opinion for the recommended method for generation of each pollutant. Each panel member was given three working days to complete this assignment. The panel meeting was then concluded.

Upon receipt of the five data sheets from each panel member, a consensus comparative ranking of methods for each pollutant was determined and is presented in Tables 4-8 through 4-12.

4.4 Results

Since each of the thirteen sets of criteria presented in Table 4-6 was given an equal weight, the results of the comparative evaluation were computed by totalling the numerical equivalent of the sum of the rankings for each method and dividing by thirteen, thus giving the average numerical ranking for each method. The results of consensus opinion of the panel regarding the relative ranking of the eleven methods for each pollutant gas are summarized in Table 4-13. The method that received the highest numerical number was, in the opinion of the panel, the recommended method.

TABLE 4-7. COMPARATIVE RANKING OF METHODS FOR _____

Criteria	1	2	3	4	5	6	7	8	9	10	11
Simplicity of Method											
Equipment/Processing Requirements											
Operator Skill Requirements											
Portability											
Cost											
Development											
Apparatus											
Per Test											
Safety											
Range											
Blind Mode											
Accuracy											
Ease of Implementation											
Confidence of Success											
Maintenance											
Operational Capability											

TABLE 4-9. COMPARATIVE RANKING OF METHODS FOR NO_2

Criteria	1	2	3	4	5	6	7	8	9	10	11
Simplicity of Method	B	B	A	C	B	B	C	C	B	A	-
Equipment/Processing Requirements	C	B	B	C	B	C	C	C	B	C	-
Operator Skill Requirements	C	B	A	C	B	C	C	C	B	B	-
Portability	C	A	A	B	B	B	C	C	A	A	-
Cost											
Development	A	C	C	C	B	B	C	C	C	B	-
Apparatus	C	B	B	C	B	B	C	B	B	C	-
Per Test	B	A	A	A	B	A	B	A	B	B	-
Safety	A	A	A	B	A	A	B	C	A	C	-
Range	A	B	A	B	A	B	B	A	A	A	-
Blind Mode	B	B	A	B	B	A	B	B	B	A	-
Accuracy	A	B	B	B	A	B	B	C	B	C	-
Ease of Implementation	A	B	B	C	B	C	C	C	B	C	-
Confidence of Success	B	B	A	C	B	C	B	C	B	C	-
Maintenance	A	A	A	B	A	B	B	B	B	C	-
Operational Capability	A	C	A	A	A	C	A	A	A	A	-

- Method not recommended

TABLE 4-8. COMPARATIVE RANKING OF METHODS FOR SO_2

Criteria	1	2	3	4	5	6	7	8	9	10	11
Simplicity of Method	B	B	A	C	A	B	C	C	A	A	-
Equipment/Processing Requirements	B	B	B	C	B	C	C	C	B	B	-
Operator Skill Requirements	B	B	A	C	B	C	B	B	B	B	-
Portability	B	A	A	B	B	B	C	B	A	A	-
Cost											
Development	A	C	C	C	C	C	C	C	B	B	-
Apparatus	B	B	B	B	C	B	C	B	B	B	
Per Test	B	A	A	A	B	A	A	A	B	B	-
Safety	A	A	A	C	A	A	B	B	A	B	
Range	A	B	A	A	A	B	B	B	A	A	-
Blind Mode	B	A	A	B	A	A	A	B	A	B	-
Accuracy	A	B	B	B	A	B	B	B	B	C	-
Ease of Implementation	A	B	B	C	B	C	C	C	B	C	-
Confidence of Success	A	A	A	C	B	C	C	B	A	C	-
Maintenance	A	A	A	B	A	B	B	B	A	B	-
Operational Capability	A	C	A	A	A	C	C	A	A	A	-

— Method not recommended

TABLE 4-10. COMPARATIVE RANKING OF METHODS FOR CO

Criteria	1	2	3	4	5	6	7	8	9	10	11
Simplicity of Method	A	B	A	C	A	B	C	C	A	B	C
Equipment/Processing Requirements	A	B	B	C	B	C	C	C	B	B	C
Operator Skill Requirements	A	B	A	C	B	B	C	C	B	B	C
Portability	C	A	A	B	B	B	C	B	A	B	C
Cost											
Development	A	C	C	C	C	C	C	C	B	B	C
Apparatus	B	B	B	B	B	B	C	B	B	C	C
Per Test	A	B	A	B	A	A	B	A	B	B	C
Safety	A	A	A	B	A	A	B	B	A	B	A
Range	B	B	A	B	A	B	B	B	A	A	A
Blind Mode	B	B	A	B	A	A	B	B	B	B	A
Accuracy	A	B	B	B	A	B	C	C	B	C	C
Ease of Implementation	A	B	B	C	B	C	C	C	B	C	C
Confidence of Success	A	B	A	C	B	B	C	B	A	C	C
Maintenance	A	A	A	B	A	B	C	B	B	B	C
Operational Capability	A	C	A	A	A	C	A	A	A	A	A

TABLE 4-11. COMPARATIVE RANKING OF METHODS FOR O_3

Criteria	1	2	3	4	5	6	7	8	9	10	11
Simplicity of Method	B	C	A	C	–	B	C	–	–	–	–
Equipment/Processing Requirements	B	C	B	C	–	B	C	–	–	–	–
Operator Skill Requirements	B	C	A	C	–	B	C	–	–	–	–
Portability	C	C	B	C	–	C	C	–	–	–	–
Cost											
Development	A	C	B	C	–	A	C	–	–	–	–
Apparatus	B	C	B	C	–	B	C	–	–	–	–
Per Test	B	B	B	B	–	B	B	–	–	–	–
Safety	A	B	A	B	–	A	B	–	–	–	–
Range	A	B	A	B	–	A	A	–	–	–	–
Blind Mode	A	A	A	B	–	B	B	–	–	–	–
Accuracy	B	C	C	B	–	A	C	–	–	–	–
Ease of Implementation	A	C	C	C	–	A	B	–	–	–	–
Confidence of Success	A	C	C	B	–	A	B	–	–	–	–
Maintenance	A	B	A	B	–	A	B	–	–	–	–
Operational Capability	A	C	A	A	–	A	A	–	–	–	–

— Method not recommended

TABLE 4-12. COMPARATIVE RANKING OF METHODS FOR 1-BUTENE

Criteria	1	2	3	4	5	6	7	8	9	10	11
Simplicity of Method	A	A	A	B	B	B	-	C	A	B	C
Equipment/Processing Requirements	B	B	A	C	B	B	-	C	C	C	C
Operator Skill Requirements	B	B	A	B	B	B	-	C	B	C	C
Portability	B	A	A	B	B	B	-	B	A	A	C
Cost											
Development	A	B	B	C	C	B	-	C	B	C	C
Apparatus	B	B	B	B	C	C	-	B	B	C	C
Per Test	A	A	A	B	B	B	-	A	B	B	B
Safety	A	A	A	A	A	B	-	C	A	B	A
Range	B	B	B	B	A	B	-	B	A	A	B
Blind Mode	B	A	A	B	A	A	-	B	B	A	A
Accuracy	A	B	C	B	A	B	-	C	B	C	C
Ease of Implementation	A	B	B	C	B	C	-	C	B	C	C
Confidence of Success	A	B	A	C	C	C	-	B	A	C	C
Maintenance	A	A	A	B	A	B	-	B	B	C	C
Operational Capability	A	C	A	A	A	C	-	A	A	A	A

— Method not recommended

TABLE 4-13. SUMMARY OF COMPARATIVE EVALUATION

Method #	Pollutant				
	SO_2	NO_2	CO	O_3	C_4H_8
1	3.5	3.3	3.4	3.6	3.4
2	3.3	3.2	3.2	2.6	3.3
3	3.5	3.6	3.5	3.2	3.4
4	2.8	2.8	2.7	2.7	2.8
5	3.4	3.4	3.4	---	3.3
6	3.0	3.0	3.0	3.6	3.0
7	2.7	2.7	2.6	2.9	---
8	2.9	2.7	2.9	---	2.9
9	3.4	3.3	3.4	---	3.3
10	3.1	3.0	3.0	---	3.1
11	---	---	2.6	---	2.8

5.0 RECOMMENDATIONS

The comparative evaluation described in the preceding section focuses attention on certain methods for each pollutant that obtained a high ranking. In particular, for SO_2, NO_2, CO, and C_4H_8, the effusion, electrochemical drive, and novel permeation methods rate very high. This illustrates some of the weaknesses of both the overall organization of the methods and the ranking system. For those cases where the electrochemical source rated highest--SO_2, CO, and C_4H_8--the method utilizes electrochemical generation to force gas from a container at a known rate through a capillary. For those cases where effusion rates high--SO_2, CO, and C_4H_8--a gas mixture is maintained in a storage volume and dispensed through a capillary or valve. These methods are very similar differing only in detail. This similarity leads to a basic recommendation as follows:

> Development effort directed towards the provision of SO_2, CO, and C_4H_8 test atmosphere generators should be focused on low pressure storage cans to ship and store prepared mixtures of the required pollutants. Three dispensing mechanisms--a Freon based system, electrolytic drive, or a valved method are competitive. The freon based system is recommended due to its simplicity.

Primary problems which must be looked into during the development of such a method are the stability of the stored gases, the materials to be employed, the detailed procedures which are necessary, and the various sources of error. The effusion method is not recommended for nitrogen dioxide at this time due to its questionable stability of moderate concentrations. Thus, the gas phase titration and novel permeation methods are the only other two choices for generating concentrations of nitrogen dioxide. Of these, the gas phase titration system appears to be the most attractive, based on anticipated development costs and laboratory-proven reliability.

With respect to the one remaining pollutant, ozone, the UV generator modified for more reliable and easier operation is almost the only method which survives critical examination. The plasma discharge source received a fairly high ranking but appears to present no distinct advantages when compared to the UV generator. Since the UV ozone generator is an integral

part of the gas phase titration system, the following recommendation is made:

> Development effort directed toward the provision of test atmosphere generators for ozone and nitrogen dioxide should be combined to incorporate an "easy-to-use" UV ozone generator into the required apparatus to yield a single device capable of producing test atmospheres for both ozone and nitrogen dioxide.

It is noteworthy that certain attributes of the novel permeation method are attractive as evidenced by its consistently high ranking for all pollutants other than ozone. The fact that it ranked behind some of the other methods stems from the more complex nature of the pollutant source. As a calibration source it would have received a higher ranking. From an overall standpoint of having the capability for both calibration and quality control, the novel permeation method is attractive.

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16. ABSTRACT

The purpose of this project was to examine possible physical, physical plus chemical, and biological concepts applicable to the development of field usable test atmosphere generating devices. The primary activity for application of these devices is the round-robin survey to assess instrument/operator performance on a routine periodic basis. Ten concepts (i.e., desorption, effusion, thin film evaporators, novel permeation, radiolysis-photolysis, plasma discharge, thin films of dissolved reactants, electro-chemical films of laminated reactants, and biological generation) were examined for each of the five required pollutants (i.e., sulfur dioxide, nitrogen dioxide, carbon monoxide, ozone, and 1-butene) and a total of fifty individual discussions prepared. The program was divided into three distinct phases: 1) comprehensive literature search and preparation of technical discussions; 2) panel review of 50 discussions and 3) comparative evaluation. Of the concepts investigated, the effusion method is recommended for generating test atmospheres for sulfur dioxide, carbon monoxide, and 1-butene, while for ozone, UV generation modified for more reliable and easier operation is recommended. Gas phase titration of nitric oxide with ozone modified for field use is recommended for generating test atmospheres of nitrogen dioxide.

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17. KEY WORDS AND DOCUMENT ANALYSIS

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